Global Intercomparability in a Changing Ocean: An International Time-Series Methods Workshop

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Table of Contents

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CHAPTER 1: INTRODUCTION

Decades of research have demonstrated that the ocean varies across a range of time scales, with anthropogenic forcing contributing an added layer of complexity. In a growing effort to distinguish between natural and human-induced earth system variability, sustained ocean time-series measurements have taken on a renewed importance. Shipboard biogeochemical time-series represent one of the most valuable tools scientists have to characterize and quantify ocean carbon fluxes and biogeochemical processes and their linkages to changing climate (Karl, 2010; Chavez et al., 2011; Church et al., 2013). They provide the long, temporally resolved datasets needed to characterize ocean climate, biogeochemistry, and ecosystem change.

Several examples from different basins and regions illustrate the scientific value of these long-term data sets. Over 40 years of ecological observations in the western English Channel (Time-Series Station E1) linked observed shifts in the marine food web to North Atlantic climate variability, specifically to phase changes in the Atlantic Multidecadal Oscillation (Edwards et al., 2013). The temporal scale of these shifts was on the order of several decades, a cycle that would have gone unnoticed without a consistent and comprehensive monitoring program (Russell et al., 1971; Southward, 1995). Similarly, using 15 years of repeat measurements in the southeastern Caribbean Sea (CARIACO time-series station), Taylor et al. (2012) showed how the upwelling-favorable trade winds have diminished due to the northward migration of the ITCZ, warming the ocean and decreasing primary productivity with effects cascading through the local ecosystem. In the coastal Pacific Ocean (time-series stations IMARPE, Peru and MBARI, California), the El Niño-Southern Oscillation (ENSO) has been shown to affect primary productivity in surface waters (Chavez et al., 2011), while in the oligotrophic Pacific (Hawai'i Ocean Time-series - HOT), a shift in the phytoplankton community was reported in the early 1980s that was presumably linked to changes in the North Pacific climate system (Karl et al., 2001; Corno et al., 2007). These large-scale atmosphere-ocean interactions occur on interannual to decadal time scales, and would go largely unresolved without time-series observations.

While stationary biogeochemical time-series provide a highly resolved temporal dataset, they are relevant only at a local scale, and generally cannot be extrapolated to larger regions. However, when multiple time-series are combined, a regional and even global picture of variability can emerge. For example, the ICES Phytoplankton and Microbial Plankton Status Report 2009/2010 (O'Brien et al., 2012) consolidated 101 time-series locations across the North Atlantic and found significant *in situ* sea surface temperature trends, indicating that in the last 30 years, the North Atlantic has warmed. Similarly, they observed coherent decadal variations in phytoplankton community structure throughout the different North Atlantic time-series, such as increases in total diatom and decreases in total dinoflagellate abundances.

There is extraordinary, unexploited strength in numbers with respect to ocean time-series. Large spatial-scale analyses using many different time-series will allow us to detect and interpret linkages between climate variability and ocean biogeochemistry, ultimately improving our understanding of marine ecosystem change. However, in order to bring together datasets from different time-series, it is

important that the sampling and analytical protocols used at each site are transparent, consistent, and intercomparable. Shipboard time-series programs measure a set of core physical and biogeochemical parameters on each cruise. However, despite the fact that many biogeochemical time-series have used the JGOFS protocols as a basis for their sampling and analytical methodologies, several adaptations have been made based on local oceanographic conditions (e.g., open ocean vs. coastal) and several other factors. To date, no thorough intercomparison among time-series methodologies has been conducted at a global scale. While certified reference materials (e.g., A. Dickson's DIC standards) and consensus reference materials (e.g., D. Hansell's DOC and DON standards) that have emerged in the last decade provide a means for analytical comparability ('standardization') among time-series measurements, no certified standards exist for many of the biogeochemical measurements conducted at time-series sites (Karl, 2010; Church et al., 2013). Consequently, a significant challenge with regard to quality assurance and control (QA/QC) and data intercomparability lies in the determination and reporting of overall uncertainty (Ellison and Williams, 2012).

In a summary on the state and direction of shipboard time-series, Church et al. (2013) stated

> *"The continued successes of biogeochemical time-series programs depend on maintaining high quality, interdisciplinary measurements focused on assessing the sensitivity and resilience of ocean ecosystems to change."*

This focus is critical for ensuring that shipboard time-series data are appropriately utilized by the scientific community in assessing current and future ocean changes. Furthermore, the authors strongly suggested

> *"Developing confidence that measurements conducted at different sites are intercomparable demands that these programs continue to regularly participate in community-wide efforts directed toward standardizing methodologies and analyses."*

To address methodological approaches and data intercomparability across shipboard time-series, the International Ocean Carbon Coordination Project (IOCCP) and the Ocean Carbon & Biogeochemistry (OCB) Program jointly convened an international time-series methods workshop November 28-30, 2012 at the Bermuda Institute for Ocean Sciences (BIOS), home of the Bermuda Atlantic Time-series Study (BATS), one of the longest ship-based biogeochemical time-series. The workshop was the third in a series of workshops focusing on ship-based biogeochemical time-series that started in November 2008 (La Jolla, CA, USA) with the *Changing Times: An International Ocean Biogeochemistry Time-series Workshop* (http://www.us-ocb.org/publications/ChangingTimesRpt.pdf); this was followed by the *Sea Change: Charting the course for ecological and biogeochemical ocean time series research* (http://www.whoi.edu/sites/OCB_Time_Series, Church et al., 2013) workshop in September 2010 (Honolulu, HI, USA). However, unlike the previous two, this workshop focused specifically on the methods employed by each time-series with the aim of enhancing data comparability between sites. The workshop goals included the following:

- Review current oceanographic time-series core sampling and analytical methodologies and rationale behind protocol differences
- To the extent possible, attempt to define standardized methods applicable across time-series
- Attempt to reconcile differences in variable nomenclature
- Examine new techniques available for more accurate and simplified measurements
- Explore the roles of autonomous sensors in improving and expanding time-series measurements

- Coordinate a best practices publication to facilitate data inter-comparison across time-series sites

With representation from 17 countries and 33 time-series around the globe, the workshop convened scientists and technicians who possess an understanding of the overarching scientific goals and methodological rationale of their time-series, as well as ample hands-on experience with sample collection and analysis. The workshop opened with plenary talks that highlighted scientific insights derived from shipboard and fixed-point time-series, as well as the logistical challenges of maintaining time-series, particularly in developing countries. Participants then met in small groups to discuss shipboard sampling order and methodological approaches for the following biogeochemical parameters:

- Pigments
- In line (bow intake) measurements
- CTD parameters and discrete calibrations
- Inorganic macro- and micronutrients
- Biomass
- Inorganic carbon parameters
- Biological rates (primary and bacterial production)
- Sediment trap fluxes
- Organic matter concentrations

This report contains the results and recommendations emerging from the discussions that took place at the workshop. For shipboard sampling order, we have provided universal recommendations for the most critical samples to draw first (at any time-series), followed by guidelines for deciding on the order of remaining biogeochemical samples, which largely depend on the scientific objectives, water budgets, and a host of other scientific and logistical factors for a given time-series.

For each biogeochemical parameter, working group members ranked the most current and commonly used methodological protocols in a recommended order (best, good, acceptable) based on analytical precision, accuracy, accessibility, ease of use, and limitations. The rationale behind this tiered approach was that comparative information about method performance would

- help existing and emerging shipboard biogeochemical time-series prioritize the allocation of limited resources for different measurements by identifying the most appropriate methods based on their scientific question(s) and associated data quality needs; and
- help data users make more informed choices when comparing data sets from multiple time-series, particularly those data that were generated using different methods.

Ultimately, we hope this report will serve as a tool to facilitate data comparability and continual communication and improvement of shipboard biogeochemical time-series sampling and methodological protocols. For the sake of data continuity and clarity, we strongly recommend that no changes in time-series measurements be made without careful analysis and documentation.

More information is available on the workshop web portal (http://www.whoi.edu/website/TS-workshop/). Since the workshop, we have developed an expanded web-based global network of shipboard biogeochemical time-series (http://www.whoi.edu/website/TS-network/), which includes detailed information about parameters being measured and methods being used at shipboard biogeochemical time-series sites.

CHAPTER 2: BIOGEOCHEMICAL PARAMETERS

Prior to the workshop, all participants provided detailed information on the parameters they measure and the methods (and associated references) they use. This information was summarized for all time-series, and the cited methods were compiled on the workshop website. Participants were divided into nine (9) working groups before the workshop and tasked with familiarizing themselves with the methods used for their respective set of biogeochemical parameters. This ensured that discussions held during the workshop were as informed and productive as possible. Each working group comprised representatives from multiple time-series, and focused on a different set of biogeochemical parameters, including the following:

- Pigments
- In line (bow intake) measurements
- CTD parameters and discrete calibrations
- Inorganic macro- and micronutrients
- Biomass
- Inorganic carbon parameters
- Biological rates (primary and bacterial production)
- Sediment trap fluxes
- Organic matter concentrations

Initially, participants divided up into smaller groups to discuss and compare shipboard order of sample collection for each site. Participants then assembled into the nine (9) working groups to discuss sampling and analytical protocols for each set of biogeochemical parameters.

With a focus on sampling, standardization, nomenclature and data reporting, and quality assurance and control (QA/QC) protocols, the working groups compared established methods and developed a consensus ranking of methods (best/good/acceptable) for each parameter. With the recognition that not all time-series can easily adopt the best method for each parameter, working groups identified metadata (method details and descriptors) that would facilitate comparison of data derived from different methods. Working groups also discussed newly emerging technology that might improve data precision and accuracy in the future and how to ensure continuity and intercomparability of datasets as methods are improved. In the following ten sections, we summarize the outcomes and recommendations of these group discussions on sampling order and methodological approaches for the aforementioned biogeochemical parameters.

2.1. SHIPBOARD SAMPLING ORDER

Introduction

Following the smaller group discussions, workshop participants met in plenary to discuss the order in which biogeochemical samples are drawn from sample bottle(s) once the rosette is secured on the ship's deck. While there was general consensus about which variables should always be extracted first (gases, carbon, organics), the order of others depended largely on the scientific focus and logistical constraints (e.g., available water budget vs. sample priority) of individual time-series. For example, a physical parameter-oriented time-series program may prioritize collecting salinity samples first, while a carbon-oriented program may seek to collect carbon samples first. Each time-series should thoroughly document their sampling order and the rationale behind it, including any historical information on sample order testing conducted at the time-series. *Most importantly, the order of sampling should be consistent through time*. If changes in sampling order must be made, they should be well documented, including the rationale behind the change.

Recommended order of sample draw

The order of sample drawing recommended below takes the following into consideration: Minimization of loss and/or gas exchange (volatile gases, inorganic carbon parameters) and minimization of contamination (organics), which increases with handling of the rosette sample bottle output. The order in which all other samples are drawn depends on the importance of the sample relative to the water budget and scientific objectives of the time-series.

1. **Gases:** The recommended order of gas sampling is as follows:
    a. Transient tracers - tritium (^{3}H), helium, CFCs
    b. Reduced gases - CH_4, N_2O, H_2S, DMS, etc.
    c. Dissolved oxygen

2. **Inorganic carbon parameters:** The recommended order of sampling is as follows:
    a. DIC
    b. pH
    c. TA
    d. DIC ^{13}C

3. **Organics:** The recommended order of sampling is as follows:
    a. DOC/TOC, TDN
    b. CDOM
    c. Other dissolved organic nutrients (e.g., nitrogen, phosphorus)

Sampling order of the biogeochemical parameters listed below varied across different time-series. Most of these parameters are less sensitive to loss, contamination, and/or gas exchange than the ones listed above, but some warrant special attention and consideration.

4. **Nutrients:** These include all dissolved inorganic nutrients (ammonium, silicate, nitrate, nitrite, and phosphate). For most sites, nutrient samples are drawn after organic matter, and ammonium should be drawn first, given its susceptibility to contamination.

5. **Salts:** Salinity samples can be found in the extraction order as early as right after the gases, or as the last drawn (highly site- and objective-dependent) -
    a. it has been suggested (anecdotally) that even short lengths of time inside the rosette sample bottles may adversely affect the salinity content of the sample
    b. salinity can be used as a marker of "mis-trips"; therefore, it is recommended that salinity be measured in all bottles (this is generally the case)

6. **Particles:** These include samples for particle absorption and particulate organic and inorganic matter -
    a. time-series setting typically determines particulate content of samples - e.g., coastal waters are richer in particulates than open ocean systems
    b. to avoid settling biases in systems with high particle load, it is best to double trip rosette sample bottles, one to be sampled directly for gases and the other to be transferred into a carboy and well mixed just prior to taking particle samples

7. **Pigments and rate measurements:** These include chlorophyll *a* fluorescence, pigments for HPLC, samples for phytoplankton taxonomy, and samples for primary production incubation experiments (in situ or on deck) -
    a. some time-series perform a separate cast for rate measurements
    b. many time-series draw rate measurement samples just after gases due to ship time constraints and length of time required for incubations; regardless of incubation time, incubations should be initiated at the same time of day
    c. pigments should be collected at the same time of day
    d. consider the potential impact of post-collection particle settling on phytoplankton density estimates

8. **Bacteria/DNA:** Some time-series measure bacterial abundance/production and collect samples for DNA extractions (characterization of community composition) –
    a. when using radioisotopic substrates to assess production rates, care must be taken to avoid contamination by trace amounts of organics (i.e. fingerprints), which may result in isotope dilution and rate underestimations
    b. these variables may be affected to a certain extent by particle settling

General sampling considerations and recommendations

- Above all, use common sense – e.g., do not lower the rosette into the water when there is bilge/garbage release; do not draw samples when there is painting or other work involving solvents, chemicals, etc. on deck; do not smoke in the vicinity of sample-drawing area; if your sample tubing has or requires grease, do not draw your sample before the organics, as this will contaminate them
- Some time-series must do multiple casts to sample all desired parameters, and these casts can occur over the course of several hours, often resulting in an offset between casts due to changing water masses, time of day, etc.; as a result, time of cast or individual sample collection (including time zone – i.e. local, GMT, etc.) needs to be carefully recorded in the metadata, as this information is critical to data interpretation
- After the rosette is secured on deck, check for sample bottle leaks and record results, concomitantly ensuring all personnel are apprised
- Record any mis-trips or problems with the bottles in the metadata
- Keep rosette sampling bottles out of direct sun and weather to minimize heating, dilution, and potential alterations to both physical and biogeochemical parameters
- Field precision should be based on replicate samples drawn from different rosette bottles tripped at the same nominal depth
- To assess potential effects of sampling order on a specific parameter or set of parameters, do a comparison experiment - trip two or more rosette sampling bottles at the same depth, draw samples in a different order, and compare measurements (see Section 3.1)

2.2. PIGMENTS (see also Section 2.6. BIOMASS)

Introduction

Working group members: R. Letelier (lead), V. Lutz (lead), M. Cañon Paez, O. Kawka, J. Ledesma, J. Rojas, K. Simpson

This working group discussed methods for measuring pigments. The unit most commonly used is mass of pigment per unit volume. There are no known issues with nomenclature across time-series sites.

Overall recommendations

- Consistency of sampling time (day vs. night) is important in order to minimize variability resulting from photoacclimation; night-time sampling is recommended over day-time sampling
- Keep samples in the dark or in low light conditions during collection, filtration, and storage (until analysis)
- Record exact volume of water filtered, as this ultimately determines reported pigment concentration
- Replicates of the same sample and field replicates from the same or different rosette bottles (from one or two depths on each cruise) should be routinely collected and analyzed to quantify analytical precision and constrain measurement variability, respectively
- Extraction efficiency is dependent upon cell types (phytoplankton composition) and is therefore site-specific (e.g., diatoms and dinoflagellates are easily extracted with acetone, whereas small coccolithophore cells with heavy cell walls are more difficult to extract, and thus require a stronger solvent like methanol or a longer extraction time)
- Dimethyl sulfoxide (DMSO) is the most effective (highest recovery) solvent for Chl *a* extraction but, because of its high toxicity, it is not recommended for routine measurements
- Redundant measurements (e.g., fluorometry and HPLC) can help assess measurement quality and provide the means for comparison with laboratories and time-series sites that use either HPLC or fluorometric methods
- Time-series sites that make their own HPLC measurements should periodically send a subset of replicate samples to a centralized, well-recognized laboratory for intercalibration and external evaluation
- Maintaining detailed metadata is critical, as small differences in protocol, even within the same method, can have significant effects on the final results; specific metadata recommendations include:
    - Provide sufficient detail and rationale for chosen methodology (e.g., extraction method, solvent, level of detection, potential caveats, etc.)
    - Report precision, replicates, analysts' names and contact information to ensure that end user can contact appropriate person with questions
    - Report both standard deviations and uncertainties due to external factors such as natural variability in phytoplankton community composition

2.2.1. Chlorophyll *a* (Chl *a*)

Ranking of available methods

BEST	HPLC (best method) plus fluorescence - most commonly used approach
GOOD	Fluorescence - Precision is ~5%
ACCEPTABLE	Spectrophotometry (absorption) – low sensitivity, not appropriate for oligotrophic samples

Sampling and analytical considerations

- HPLC should be kept frozen in an ultralow freezer (~-80°C), or in liquid nitrogen until analysis to avoid pigment degradation (Refer to Wright et al., 1997).
- If using only the fluorometric method for Chl *a* determination, it is advisable to run spectrophotometry and/or HPLC on a small set of replicate samples to ensure the accuracy of measurements
- When using the spectrophotometric method, the trichromatic equation (Jeffrey & Humphrey, 1975) is recommended to derive chl *a* concentration (see also http://www.aoml.noaa.gov/ocd/sferpm/louda/louda_chl_compare.html)
- Fluorescence by Chl *b* and Chl *c* interferes with Chl *a* fluorescence spectra – i.e. acidification increases (decreases) Chl *b* (Chl *c*) fluorescence, resulting in underestimation (overestimation) of Chl *a*; thus, the relationship between HPLC and fluorometry often deviates from 1:1
- Phaeopigment measurements obtained from fluorometric techniques are often overestimated (underestimated) due to interference from Chl *b* (Chl *c*)
- The volume filtered for Chl *a* analyses is site-dependent and should be recorded in the metadata
- Solvent choice depends on phytoplankton composition and should be selected to maximize extraction efficiency:
    - Acetone is sufficient for systems dominated by diatoms and dinoflagellates; if acetone is used, sonication or longer extraction time may be necessary
    - Methanol works better for systems dominated by organisms with heavier cell walls (e.g., coccolithophores)
    - DMSO is the strongest and most efficient solvent, but it is not recommended for routine extraction due to its high toxicity
    - Most importantly, carefully document solvent choice and rationale in the metadata
- Analytical consistency and accuracy must be carefully monitored and recorded:
    - Routinely measure replicates of same sample to monitor precision
    - Routinely monitor fluorometer drift using secondary standards
    - Calibrate fluorometer using NASA calibration procedures (Trees et al., 2000) at least every 3 months when in use, or whenever the equipment has been moved (from one lab to another, taken to sea, etc.), or not used for a long period of time, or to evaluate lamp and photomultiplier drifts
    - Conduct regular laboratory and method intercomparison exercises
- Report all data and associated details - data quality ultimately depends on metadata; each data point should have a quality flag (e.g., good, questionable, bad) with accompanying reason for its quality designation recorded in metadata – e.g., sample was thawed, fell on workbench, etc.

- In vivo passive fluorescence is another technique for Chl *a* determination but it cannot be considered quantitative since it does not take into account changes in fluorescence yield due to photochemical and non-photochemical quenching

Available standards

- Most commonly used primary standard to perform fluorometric calibrations is the Sigma Aldrich Chl *a*; it should be measured via spectrophotometry (concentration is calculated considering an extinction coefficient of 88.15 {$lg^{-1}cm^{-1}$} for absorbance at 662 nm) prior to use in order to document actual concentration and purity; leftover standard should be stored dry (degas first with nitrogen) in the ultra-freezer
- Other standards are acceptable, but they should be made from cyanobacteria and not from spinach to avoid contamination with Chl *b*
- Secondary standards (fluorescing solid) also provide a good day-to-day reference, but regular calibration against the primary standard is still recommended

2.2.2. Other Pigments

Ranking of available methods

BEST	HPLC
ACCEPTABLE	Differential spectroscopy (spectroscopic deconvolution) – seldom used because time consuming and requires validation with HPLC

Sampling and analytical considerations

- Some pigments, namely phycobilins, are not extracted nor detected using common analytical methods
- Storage method
    - Liquid nitrogen is optimal for storing HPLC filters
    - Ultra-freezing (-80°C) is also acceptable
    - Conventional freezers should only be used for short-term (~24 hrs) storage; if this is all that is available for long-term storage, then an experimental determination of potential pigment degradation should be conducted prior to conventional freezing
    - Always record sample filtration and storage information in the metadata
- Pigment identification in chromatograms is usually based on elution time. However, confirmation of pigment identity and response factor should be carried out routinely using commercial standards or by sampling the elution of specific absorption peaks and characterizing the full absorption spectrum in a spectrophotometer

Available standards

- Sigma Aldrich Chl *a*, Chl *b*, and β-carotene are the most commonly used standards for HPLC; other pigment standards can also be purchased in solution from DHI Labs

2.3. IN LINE MEASUREMENTS

Introduction

Working group members: M. Ishii (lead), M. Telszewski (lead), N. Bates, K. Currie, B. Fiedler, S. Punshon, T. S. Rhee, A. Sutton, R. Wanninkhof

Post-meeting comments from A. Dickson (Scripps Inst. of Oceanography, Univ. of California, San Diego) have been incorporated

In line measurements pertain to automated continuous measurements and sampling from seawater intakes on research ships and ships of opportunity. In addition to providing quality data, in line measurements represent a powerful tool for instrument and technique development, as well as extending fixed-point time series. Shipboard biogeochemical time-series platforms are well suited for testing of new sensor technology, since discrete bottle samples offer ample opportunities for calibration and ground-truthing.

Overall recommendations

The quality of the ship's infrastructure with regard to in line systems (tubing, pumps) is critical. A lot of consideration was given to various aspects of the in line system:

1. Depth of sampling needs to be recorded in the metadata
    a. It is highly variable between different ships
    b. The inlet should be in the bulk mixed layer (below warm layer ≈ 1-2 m) – depth needs to be well documented
    c. Intake should be right at the bow to avoid contamination by the ship's discharges or hull

2. In line system
    a. Flow rate should be well documented (critical QC information)
    b. Transit time of water in the pipe is important and should be documented
    c. Cleaning the seawater line is a very important requirement (Juranek et al., 2010)
        i. Strainers should be installed right at the intake and should be cleaned regularly as required
        ii. Clean the seawater line with bleach every 6 months or more frequently in eutrophic waters - there are concerns regarding potential oxidation of organic matter in the line
        iii. Back flush line with freshwater whenever in port and leave filled with fresh water when seawater line not in use
        iv. Alternatively, the sample line can be stored dry between cruises

    d. Pumps
        i. Centrifugal pumps are most widely used – there are some possible issues with fluorescence measurements (induced fluorescence by agitation)
        ii. Large piston pumps are an alternative but are expensive, not well tested, and may have issues with pulsation
        iii. Jet pumps have known issues with creating bubbles

e. Material - Materials should be tested. A good way to test material sorption or desorption and biofouling issues is to stop the flow for a period of time and measure relevant concentrations right upon start-up
    i. Soft steel piping is problematic
    ii. Other steels and alloys not optimal
    iii. No strong recommendation of synthetic tubing/piping, but generally the harder materials are better for gases (Teflon is good for trace metals but less so for gases)
    iv. Long lengths of (garden) hose are not optimal for connecting system components - "conditioning" of new material is recommended

f. De-bubblers - Remove bubbles from breaking waves and pump cavitation from the seawater lines
    i. Salinometer and optical sensors/instruments that are impacted by bubbles should be placed after the de-bubbler
    ii. Effect of de-bubbler on gases is not well characterized, though it seems to be more of an issue for insoluble gases such as oxygen

2.3.1. Temperature

Ranking of available methods

BEST	A sensor with quantifiable accuracy (e.g., Sea-Bird 38, Sea-Bird 21)

Sampling and analytical considerations

Temperature measurements and control

- With all temperature sensors, do not rely solely on manufacturers' stated accuracy; regular lab calibrations and at-sea comparisons (e.g., with CTD) are recommended
- Measuring the temperature at the inlet to determine SST (sea surface temperature) is ideal (sensor installed as close to the inlet as possible, before other instruments and technical equipment like pumps and flow meters)
    1. If temperature at the inlet can't be measured directly, a hull-mounted temperature sensor or a surface temperature from the CTD is acceptable (sufficient CTD casts should be taken to ensure robust interpolation)
    2. Bucket sampling is not recommended unless no other method is available
    3. Back-calibration to determine SST upon installation of the inlet temperature sensor is recommended
- Short distances between seawater inlet and instrument/lab, as well as thermal insulation of seawater line is recommended to minimize temperature changes
- Temperature measured at instrument/in the lab is fundamental to ensure data quality and correction for analysis of temperature-dependent parameters such as pCO_2 and pH
    1. Temperature sensors (platinum resistance thermistor) are very stable over years, but annual calibration is recommended (ideally to 0.01˚C but 0.02˚C is acceptable)
    2. Manufacturer calibration is ideal but more expensive
    3. Lab calibrations are completely acceptable

2.3.2. Conductivity (Salinity)

Ranking of available methods

BEST	A sensor with quantifiable accuracy (e.g., Sea-Bird 45, Sea-Bird 21)

Sampling and analytical considerations

- Take discrete in situ samples for calibration. Calibration should be performed against salinity standards using a functioning salinometer. These data should be used to calibrate the CTD cast as per the CTD manufacturer's instruction (annual factory calibration is typically recommended)

2.3.3. pCO_2

Ranking of available methods

BEST	It is desirable to measure seawater pCO_2 with an uncertainty (95% confidence) of ±2 µatm. Currently, this requires use of an equilibrator-based approach, in which the CO_2 level in the headspace gas is subsequently measured via an IR- or GC-based approach calibrated with at least 2 non-zero CO_2-in-air standard gases that are traceable to the WMO Mole Fraction Scale for CO_2.

Emerging technology

- Cavity Ring-Down Spectroscopy
    1. Much more expensive
    2. Potential for minimization of calibration/standardization issues
- Lower cost IR-based technology (e.g., LICOR 840)
- IOCCP has a list of manufacturers on their website at http://www.ioccp.org/instruments-and-sensors - pco2. Recommendations regarding the use of new platforms and sensors for pCO_2 measurements will be available soon

2.3.4. pH

Ranking of available methods

BEST	Spectrophotometric method (e.g., Sunburst Systems Autonomous Flow-Thru, or AFT-pH)

Sampling and analytical considerations

- Report standards, temperature, and pH scale (NBS, SWS, total hydrogen) in metadata
- Impurities in commercially available indicator dyes have been problematic in spectrophotometric pH determination (Yao et al., 2007); colored impurities introduce a pH-

dependent error that can be >0.01 pH unit; the level of impurity and the associated error can vary between dye batches from the same or different manufacturers

- The indicator dye used in the pH measurement must be documented in the metadata:
    - *m*-cresol purple is more appropriate for open ocean water column (surface to deep) pH measurements, whereas thymol blue is more appropriate for surface seawater (in line measurements; Zhang and Byrne, 1996; Aßmann et al., 2011)
    - Measurements made using different indicator dyes (at different sites) should be noted, as this may limit the comparability of the pH data
- Use of purified indicator dyes for pH determination is optimal; however, it is recognized that purified indicator dyes are not widely available:
    - See recent studies on purification of *m*-cresol purple (Patsavas et al., 2013 via flash chromatography; Liu et al., 2011 via HPLC) and cresol red (Patsavas et al., 2013 via flash chromatography)
    - There is a suggestion that thymol blue can be obtained in a sufficiently pure form but this has not been extensively tested
- Careful attention must be paid to calibration of indicator dyes and inherent uncertainties in the calibration procedure should be documented:
    - Currently, only *m*-cresol purple has been adequately calibrated in pure form (e.g., Easley and Byrne, 2012)
    - Calibrations based on unpurified dyes are available for cresol red and thymol blue
- The pH perturbation correction required in the spectrophotometric method must be done as carefully as possible, as this can contribute to overall measurement uncertainty
- pH reference materials are needed for routine quality control of pH measurements

Emerging technology

- Ion sensitive field effect transistor (Durafet) sensors – this is a very active and rapidly developing field, but more work is needed to ensure appropriate calibration procedures before they are ready for widespread use

2.3.5. Total Dissolved Inorganic Carbon (DIC)

Emerging technology

- IR-based discrete sampling instruments
- Spectrophotometry (Wang et al., In press; Wang et al., 2007)
- Robotic Analyzer for the TCO_2 System (RATS) (Sayles and Eck, 2009)

2.3.6. ^{13}C of DIC

Emerging technology

- Cavity Ring-Down Spectroscopy (CRDS) analyzer (Becker et al., 2012)

- Accuracy of 0.33 per mil (based on comparison against reference measurements of individual water samples via isotope ratio mass spectrometry)

2.3.7. In vivo Fluorescence

Ranking of available methods

BEST	Fluorometer (e.g., WetLab ECO, Turner 10-AU-005)

Sampling and analytical considerations

- Systematic calibration procedure and protocols are critical
- Routine calibration involves comparison of fluorometer measurements to extracted chlorophyll obtained from discrete bottle samples
- The ratio of Fluorescence:Chl *a* varies with phytoplankton type and photoacclimation, so the required frequency of discrete calibration sample collection may vary from site to site, depending on spatiotemporal phytoplankton distribution
- Calibration frequency should capture diurnal variability (2x/day), at a minimum
- Fluorescence reported as RFU (relative fluorescence units)
  Uncalibrated measurements provide qualitative information on spatial and temporal variability which is useful if the fluorometers are frequently cleaned

2.3.8. Oxygen

Ranking of available methods

BEST	Sea-Bird IDO, Aanderaa Optode, JFE Advantech RINKO III

Sampling and analytical considerations

- Calibration
  - Pre-cruise/lab calibration is required
  - Frequent in-situ calibration required (against Winkler samples) as some sensors might deviate even when pre-calibrated (Bittig et al., 2012)
  - Comparison to the CTD bottled data is acceptable
- Units
  - Use of µmol/kg of seawater is recommended
  - Use of µmol/L and mL/L are acceptable
  - Use of mg/L is not recommended

2.4. CTD PARAMETERS AND DISCRETE CALIBRATIONS

Introduction

Working group members: C. Chandler (lead), A. Körtzinger (lead), D. Grundle (rapporteur), A. Cianca, M. Conte, R. Johnson, M. Kampel, Y. Takatani

Overall recommendations

- CTD unit (Sea-Bird units are most popular)
- Dual sensor configuration (SBE 35 preferred), if possible
- Full depth calibrations with salinity and DO
- Report number of scans per record in the final pressure binned profile data
- While frequent calibrations are recommended (e.g. 6-9 month manufacturer calibration for each CTD sensor; pressure can be every 2 years), this may not be realistic, particularly for time-series in developing nations.
- For those time-series sites that are unable to ship out their instruments for calibration, opportunistic calibration - e.g., "calibrations of opportunity" might be more feasible and could be arranged with traveling scientists whose instruments have been manufacturer-calibrated.
- Intercomparison of CTD calibration facilities

Ranking of available methods

Working group members focused on vertical casts and did not discuss moored mode.

BEST	CTD units with dual sensor configuration if possible
GOOD	Reversing thermometers on ships of opportunity

Recommended (most popular) CTD units:

- Sea-Bird 911+ on conducting cable
- Sea-Bird 25
- Sea-Bird 19+
- Sea-Bird 35 (high accuracy temperature sensor)
- IDRONAUT

Recommended (most popular) sensors:

- Sea-Bird 43 for profile oxygen
- Optodes typically used for mooring deployment may be best for low-oxygen environments
- WET Labs and Chelsea Technologies for fluorescence
- WET Labs for Beam Attenuation

Sampling and analytical considerations

The working group members discussed best practices for CTD deployment and came up with the following recommendations:

- Lower CTD to 10 meters, let equilibrate for 5 minutes, then raise back to surface and begin downcast
- Lowering speed a maximum of 60 meter/minute in deep water
- On the upcast, stop the rosette for 1-2 minutes before each bottle fire to allow for equilibration

Available standards

Discrete samples:

- Salinity: OSIL (standard seawater), recommend every 30 samples
- Oxygen: Potassium iodate from OSIL or CSK (equivalent quality, different cost)

Data processing and calibration:

- Seasoft commonly used for initial processing, but not by all time-series (e.g., HOT uses their own software)
- Most sites use local software routines to perform calibrations based on comparisons between discrete sample- and sensor-based measurements

Nomenclature

- Pressure (decibars)
- Depth (meters) [a few sites derive and report depth]
- Temperature (°C, IPTS 90)
    - single temperature measurement reported
- Salinity (SAL78, PSU[1])
- Dissolved oxygen (DO) µmol/L, mL/L or µmol/kg
    - Record draw temperature immediately after DO sample
- Beam attenuation coefficient (BAC) (meter^{-1})
- Fluorescence (RFU) (relative fluorescence; no units)

[1] While Practical Salinity S_P (PSS-78) is the measured variable that is recorded in databases, the Thermodynamic Equation of State of seawater (TEOS-10) uses Absolute Salinity S_A (calculated variable) as the salinity argument for the thermodynamic properties of seawater (see IOC et al., 2010).

2.5. INORGANIC MACRO- AND MICRONUTRIENTS

Introduction

Working group members: K. Johnson (lead), H. Benway (lead), M. Erickson, K. Björkman, M. Honda, J. Olafsson, M. Blum, D. Turk

Overall recommendations

This working group made the following overarching recommendations to ensure comparability and consistency of nutrient data across time-series:

- Need community-wide evaluation exercise to compare available standards - SCOR working group proposal to address global nutrient data intercomparison and history of development of nutrient standards was submitted but not funded; evaluation should, nevertheless, be pursued
- More community consensus is needed on how individual time-series monitor internal consistency (precision)
- More community consensus is needed on how individual time-series monitor accuracy (external evaluation samples)

2.5.1. Macronutrients and Low-Level Macronutrients

Ranking of available methods

Macronutrients

BEST	Autoanalyzer
ACCEPTABLE	Manual spectrophotometric analysis ok for PO_4, SiO_4

Low Level Macronutrients

BEST	NO_3 + NO_2: Chemiluminescence (Cox, 1980; Garside, 1982) PO_4: Magnesium-induced co-precipitation (MAGIC) (Karl and Tien, 1992) NH_4: Fluorescence (Holmes et al., 1999)

Sampling and analytical considerations

Sample collection and filtering:

- If using tubing, place on rosette bottle – rinse with sample 2-3 times before filling, leave head space if freezing*
- Disposable scintillation vials (single use) are best, but if reusing vials (polyethylene), acid-wash in between uses
- Filtering of nutrients is site-dependent – i.e. filtration is typically required in more turbid and/or productive waters. However, extra sample handling increases potential for contamination. If

there is uncertainty regarding the potential impact of particles on nutrient measurement, comparisons should be done between filtered vs. unfiltered samples over a representative timeframe that includes periods of high and low particle concentration in the water.

- Cleanest filtration is with teflon syringes with nucleopore polycarbonate filters (0.45 µm); be sure to measure filter blanks (humic blanks needed in coastal regions with high humic content)
- Cartridge filters often used for multiple casts or for standard seawater collection to remove critters

Sample handling and preservation:

- Samples should be kept in the dark
- Refrigerate if running on ship
- Freeze upright if longer than a few hours – *Caution: samples with high silicate concentrations (>20 µM, typical of deep water samples) should be refrigerated, never frozen; frozen PO_4 samples should be run within 6 months-2 years
- Poison with $HgCl_2$ – Caution: can affect PO_4 measurements and reduce efficiency of Cd column

Carrier solutions – very important to document what is being used:

- Low-nutrient seawater (OSIL or user-collected) – optimal, especially for low-level methods, which require the cleanest blanks possible
- Artificial seawater (different recipes affect different nutrients in different ways, all not necessarily nutrient-clean)
- Milli-Q (need to document how refractive index is determined)
- Need to monitor all carrier solutions (baseline drift)

QA/QC and data reporting - It is critical that time-series sites document their QA/QC procedures in their metadata to facilitate data intercomparison:

- How often are QA/QC samples run at time-series sites? Need to routinely evaluate internal consistency (precision)
- How often are external evaluation samples run at time-series sites? Need to routinely run performance evaluation samples and compare across time-series (accuracy)
- Linearity of calibration standards (e.g., linear vs. quadratic curve fitting) – this strongly impacts the results and should be well documented

Available standards

- Ocean Scientific International (OSIL; http://www.osil.co.uk/Resources/NewsArticles/tabid/114/articleType/ArticleView/articleId/275/The-Development-of-Seawater-Standards-for-Dissolved-Nutrients.aspx) – products include low-nutrient seawater, marine nutrient standard kits, and performance evaluation samples to compare across time-series

- Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME: Topping, 1997; http://www.quasimeme.org/) – biannually send performance evaluation samples to laboratories for an annual fee
- Kanso RMNS – private Japanese company to prepare nutrient standards from North Pacific (high Si) www.kanso.co.jp/eng/production/price.html ~$110/100 mL bottle
- Wako consensus standards – SRP, NO_3+NO_2, SiO_4
- Need consensus on universal best practices for preparation of secondary standards (from more expensive primary standardsq)

Emerging technology

- NH_4 – recent work in low-oxygen regions and subsequent characterization of ANNAMOX processes has prompted the development of alternative analytical techniques over traditional spectrophotometric methods to increase precision – e.g., OPA (orthophthaldialdehyde, sodium sulfite, and sodium borate) with fluorescence (Holmes et al., 1999)
- PO_4 – malachite green (higher sensitivity than molybdenum blue method)
- NO_3 – ultraviolet (UV) methods (e.g., ISUS – In Situ Ultraviolet Spectrophotometer); error the same over entire concentration range, so not viable at low concentrations, optimal for assessing oceanographic conditions while cruising
- NO_3 reduction - less toxic alternatives (e.g., enzymatic reductase) are being investigated as potential replacement for cadmium (Cd)

Nomenclature and units

The working group members discussed some of the commonly used nomenclature for different nutrients and determined that time-series need to carefully document the following distinctions in their metadata:

- **Nitrate:** NO_3, NTRA for nitrate (instead of NO_3) (Argo)
- **Nitrate plus Nitrite:** NO_3+NO_2, sometimes reported as just NO_3, but NO_2 is reported separately by some time-series, particularly in highly productive NO_3-reducing regions
- **Ammonium:** NH_4^+
- **Phosphate:** PO_4^{3-} vs. soluble reactive phosphorus (SRP) (SRP is what is actually measured)
- **Silicate:** SiO_4, dissolved orthosilicic acid
- **Units:** µmol/kg, µmol/L are both acceptable

2.5.2. Micronutrients

Ranking of available methods

The working group only discussed iron (Fe). Many time-series do not have a long history of Fe measurements because they used to be difficult to make. However, the methods have greatly improved and this has become a much more routine measurement. A comprehensive Fe method comparison exercise was recently conducted (Johnson et al., 2007, SAFe). The results of this study suggest that most of the current methods for Fe analysis are comparable. Careful sample collection and preparation (acidification) are the key to achieving good measurements (see below).

BEST	Automated shipboard: -Flow Injection Analysis (FIA): Spectrophotometry, Chemiluminescence -Cathodic stripping voltammetry (CSV)
GOOD	Laboratory shore-based: -Graphite furnace atomic absorption spectroscopy (GF-AAS) -Inductively Couple Plasma Mass Spectrometry (ICP-MS)

Sampling and analytical considerations

- Use trace metal rosette (powder-coated, external closure bottles rather than Niskin); bottles need to be cleaned with acid (HCl) and surface seawater before sampling
- Let water flow for awhile prior to collection
- Filter samples if necessary (see recommendations on filtering above) and acidify
- Use clean (laminar flow) hoods

Available standards

- SAFe (Johnson et al., 2007)
- GEOTRACES

2.6. BIOMASS (see also Section 2.2. PIGMENTS)

Introduction

Working group members: C. Carlson (lead), L. Lorenzoni (lead), M. Church, R. Goericke, D. Kim, M. Lomas, F. Tapia, L. Valdes

This working group focused on methodologies for bacteria/viruses, micro/nanoplankton, picophytoplankton, phytoplankton, and zooplankton. Biomass is generally expressed in mass carbon per unit volume; but, for the most part, the methods involve direct measurement of cell abundance or some proxy such as pigment to estimate biomass. These direct measurements require the use of a conversion factor (i.e. carbon conversion factor) to obtain biomass estimates. These conversion factors can vary significantly across microbial populations and with varying nutrient and light levels, so care must be taken to assess the most appropriate conversion factors. Many of the methods described below are site-specific, as coastal time-series may have different needs than open-ocean time-series.

Overall recommendations

- When possible, as a cross-check, use two methods to measure each biomass component
- When purchasing a flow cytometer, be sure to select a model that is appropriate for the type of system and organisms you are measuring, keeping in mind that flow cytometry is not the best way to quantify larger eukaryotic cells
- Sites that make multiple biomass measurements should report all related parameters to facilitate data use and interpretation; specifically, labs should report the measurements used to calculate biomass - just reporting µmol C/L is not as useful as providing the measurements (e.g., cell abundances) and conversion factors, as well as assumptions used to compute biomass
- When changing a method, careful testing and documentation is recommended, including data validation between old and new techniques

Comments on standardization

While there are no real standards for biomass, which is based on an assumed carbon:biovolume (cell abundance counts) conversion, time-series sites can develop in-house standards for cell abundance counts. For flow cytometry, archiving a large set of samples in small aliquots for use in daily runs may serve as a means of in-house standardization of cell abundance counts. Consensus standards (archived samples that are exchanged between labs) are also recommended. There are inherent operator errors in all of these measurements, so it is important that there is technician overlap between counts.

2.6.1 Bacteria and viruses

Ranking of available methods

BEST	Epifluorescence microscopy - Note this is system-dependent and some environments require a more sensitive technology like flow cytometry to separate bacteria from *Prochlorococcus*
GOOD	Flow cytometry – depending on FCM model and laser, this method could be unreliable for counting viruses

Sampling and analytical considerations

- Recommended filter is blackened 0.2 μm polycarbonate. Pre-blackened filters are available from a variety of vendors, but changes in the dye used during manufacturing has led to issues of unacceptable masking of microscopic images; therefore, it is recommended that the polycarbonate filters be stained in house using Irgalan Black dye
- Coastal time-series sites may need to use microscopy due to interference from detritus
- Stains are choice of the user and application (commonly used stains include DAPI, SYBR Green, Acridine Orange, Hoeschst); Acridine Orange can lead to non-specific binding and should be avoided in systems with a lot of detritus; some time-series have documented differences in abundance estimates using different stains (e.g., HOT with SYBR Green vs. Hoeschst); further investigation of this via a comprehensive comparison study is recommended

2.6.2. Micro- and nanophytoplankton

Ranking of available methods

BEST	Microscopy (autofluorescence) - proflavin is recommended, but this can be site-specific
GOOD	Flow cytometry - this will only separate the micro/nanoplankton into size fractions based on forward and side scatter
ACCEPTABLE	HPLC - this will determine the presence /absence of groups (lower level of detection); refer to PIGMENTS section for other recommendations on this methodology

2.6.3 Picophytoplankton

Ranking of available methods

BEST	Flow Cytometry
GOOD	Epifluorescence microscopy - will underestimate weakly fluorescent cells like *Prochlorococcus* in high light environments
ACCEPTABLE	HPLC - this will determine the presence/absence of groups (lower level of detection). Refer to the PIGMENTS section for more recommendations on this methodology

Sampling and analytical considerations

- For flow cytometry, access to liquid nitrogen or a -80°C freezer is recommended for flash freezing
- Filter pore size is generally 0.2 μm; some stains will mask weakly autofluorescent cells
- Where available, image analyses can improve signal-to-noise ratio of weakly autofluorescent cells

2.6.4. Total Phytoplankton

Ranking of available methods

BEST	Chlorophyll fluorescence: This is an indirect measurement of phytoplankton biomass, but the most widely used amongst time-series sites. Refer to the PIGMENTS section for detailed recommendations on this methodology
GOOD	Epifluorescence microscopy
ACCEPTABLE	Microscopy (inversion chamber) and taxonomy

Sampling and analytical considerations

- Methodologies regarding types of extraction and solvents to use will be site-specific, so careful reporting of metadata is critical; see Pigments section for details
- CTD fluorometer should be regularly calibrated against bench-top chlorophyll fluorescence

Emerging technology

- Submersible instrumentation that combines imaging and flow cytometry (e.g., Flow Cytobot) can be used for larger phytoplankton

2.6.5. Zooplankton

Ranking of available methods

BEST	Net tows - flow estimation can be done either with an electronic or mechanical flow meter.
GOOD	VPR or other video recording/ID device
ACCEPTABLE	Acoustics - justifiable for larger organisms (multi-frequency) and must be backed by tows; can cover large spatial scales

Sampling and analytical considerations

- Methodologies will be site-specific, so carefully reporting of metadata is critical
- Recommended mesh size for net tows is 200 μm: Mesh size will strongly influence the organisms captured, so very important to document mesh size
- Net size will depend on the ship available for the tow
- Net tow type is site-dependent - either oblique or vertical (vertical collects less material)
- Speed of oblique tow depends on mesh size – e.g., 1 knot is the recommended speed for mesozooplankton tows, but it is not universally defined and is very assembly- and site-specific
- Paired day-night tows are recommended; alternatively, the tows should always be conducted during the same time of day
- For net tows, a time/depth recorder integrated into the net is recommended to obtain information about the tows
- Zooplankton samples should be split with a Folsam splitter on land (after cruise), never on the ship due to potential biases introduced by ship's motion
- Dry weight is recommended over displacement volume for net tow analysis; the latter has known issue with jellies
- For dry weight analysis, refrigerate sample and process as soon as possible (within a day); alternatively, fix with formalin and wait 8 weeks prior to processing for weight stabilization, as formalin induces weight loss

Emerging technology

- Individual zooplankter identification tools
    - Video Plankton Recorder (VPR)
    - SIPPER (Shadow Image Particle Profiler Evaluation Recorder)
    - Zoocam
    - ZooScan
- Zooplankton counts
    - Optical Plankton Counter (OPC or LOPC) - can have difficulties distinguishing marine snow from zooplankters

2.7. INORGANIC CARBON PARAMETERS

Introduction

Working group members: N. Bates (lead), A. Körtzinger (lead), D. Turk, M. Ishii, J. Olafsson, L. Medina, R. Wanninkhof, Y. Takatani, H. Benway, K. Currie, S. Punshon, A. Cianca, K. Simpson, K. Johnson, T. Rhee, A. Sutton, B. Fiedler

Post-meeting comments from A. Dickson (Scripps Inst. of Oceanography, Univ. of California, San Diego) have been incorporated

Overall recommendations

- Detailed methodological best practices manuals exist for inorganic carbon parameters (e.g., Dickson et al., 2007)
- While coastal ocean samples can be analyzed using the same techniques that are used to analyze open ocean samples, the concentrations and degree of DIC variability observed in coastal waters might require alternate methods that are accompanied by larger measurement uncertainty; these techniques are often considerably less expensive, thus allowing more measurements to be made with limited resources, but more work is needed to develop standard operating procedures (SOP) for such alternate methods and a clearer understanding of associated uncertainties
- A common theme throughout the report is the goal of global intercomparability of measurements. For inorganic carbon, measurements should be traceable to a common stated reference (where the measurement can be traced to a reference through a documented chain of calibration) with the goal of collection of a coherent datasets (despite being made by different groups, using different methodologies, etc). Adequate quality control documentation is essential to this goal and includes assessment of measurement uncertainty, with the knowledge that there is often an inverse relationship between costs of analytical techniques and measurement uncertainty
- The precision estimates reported here generally reflect precision obtained under "repeatability" conditions. Repeatability is the closeness of agreement between independent results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratory, and over short intervals of time). Reproducibility estimates are based on independent results obtained with the same method on identical test material, but under different conditions (different operators, different apparatus, different laboratories, and/or over different intervals of time), and tend to be higher than repeatability
- The accuracy estimates reported here essentially reflect the best case scenario for carbon measurements, which includes well maintained analytical equipment, well tested methods with established QA/QC procedures, and well trained personnel

Seawater Inorganic Carbon parameters:

<u>Directly measurable parameters</u>

- Total Dissolved Inorganic Carbon (i.e., DIC, C_T, or TCO_2)
- Total alkalinity (TA or A_T)
- pCO_2 (partial pressure of CO_2) or fCO_2 (fugacity)

- pH
- DIC-^{13}C

Computed parameters

- $[HCO_3^-]$
- $[CO_3^{2-}]$
- $CaCO_3$ saturation state i.e. $\Omega_{calcite}$, $\Omega_{aragonite}$

2.7.1. Total Dissolved inorganic carbon (DIC)

Ranking of available methods

BEST	Coulometry (0.05% precision; 0.1% accuracy) – set-up and measurement time is longer, resulting in more costly measurements
GOOD	Infrared-based detector (0.05-0.2% precision; 0.1-0.2% accuracy) – good for small volume samples

Sampling and analytical considerations

- Dickson et al. (2007) describe detailed state-of-the-art analytical methods for open ocean measurements; due to the variability of coastal waters, alternate methods with different but acceptable precision and accuracy may be utilized
- Capability testing of newer generation coulometric systems is needed; the optimal coulometric method is based on older detectors (e.g., UIC 5011), with rigorous testing of newer detectors (e.g., UIC 5014/5015, etc.) underway
- A well tested SOP, including a universally adopted calibration procedure, is needed for infrared systems
- Potentiometric titration (open-cell) can yield a 0.05-0.2% precision for DIC at lower cost but the inaccuracy is high (0.5-1% accuracy) as DIC measurement uncertainties are poorly understood

Available standards

- Certified Reference Materials (CRMs) are available (e.g., A. Dickson lab, Scripps Institution of Oceanography) but expensive and may thus not be practical for everyday use; regular use of CRMs reduces measurement uncertainty
- Need to establish universal practices for preparation and application of secondary standards from CRMs
- DIC concentration of standards should bracket the concentration range of your samples – e.g., Na_2CO_3 standards of varying DIC content
- Recommend CO_2 gas calibrations for all coulometric and infrared-based systems

Emerging technology

- Spectrophotometric-based systems

- Cavity Ring-Down Spectroscopy (CRDS) systems – e.g., PICARRO; good for pCO_2 but discrete DIC needs work

Nomenclature

- Reported units: µmol/kg; µmol/L is not recommended

2.7.2. Total Alkalinity (TA)

Ranking of available methods

BEST	Potentiometric titration (Open-cell recommended over closed-cell): (0.05% precision; 0.05-0.2% accuracy)

Sampling and analytical considerations

- It is important to report standards, method used, and measurement temperature in metadata
- Special care should be taken with coastal samples
    - Filtration in high-productivity regions
    - Measure accompanying phosphate and silicate concentration to calculate nutrient contribution to TA
    - Calculate (from salinity) borate alkalinity contribution to TA
    - Consider potential influence of anoxic waters or low salinities (<20 PSU) on TA

Available standards

If utilizing secondary standards, they should ideally be prepared in a matrix of poisoned seawater that has been calibrated against a well-established CRM. Synthetic seawater (with fluoride and sulfate levels similar to natural seawater) or NaCl solutions (with ionic strength similar to sweater, ~0.7 mol/kg) can also be used. However, it is important to note that reagent-grade salts often contain an alkalinity impurity ranging from 10-30 µmol/mol NaCl used. Na_2CO_3 is not recommended for TA calibration solutions.

Nomenclature

- Reported units: µmol/kg
- µmol/L is not acceptable for TA, since TA changes in natural systems are small relative to their TA content

Emerging technology

- Spectrophotometric method for TA measurement: Although some groups are using this method, there is no well tested, universally established SOP at this time

2.7.3. Discrete pCO_2

Ranking of available methods

BEST	1. Gas chromatography (GC)-based system (0.05% precision; 0.3% accuracy) 2. Infrared (IR)-based system (0.05% precision; 0.3% accuracy)

Sampling and analytical considerations

- Water and headspace should be in complete equilibrium prior to measurement
- Measurement system should be designed to minimize the uncertainty in correcting for the change in seawater pCO_2 as it equilibrates with the headspace (e.g., gas chromatography can allow a smaller headspace/sample ratio, thus minimizing this correction and the resulting uncertainty)
- Choose calibration gases that are appropriate for the sample CO_2 levels and for the detector
- Constant temperature is critical for pCO_2 measurement and should be reported in the metadata in addition to standards and method used
- Developing systems based on lower cost IR-based detectors might facilitate measurement of this variable by more time-series
- If using IR for pCO_2 can also use for DIC

Available standards

- Compressed gas (CO_2-in-air standards)

Emerging technology

- Cavity Ring-Down Spectroscopy (CRDS) systems
    - Potential for stable calibration
    - Small air sample requirements

2.7.4. pH

Ranking of available methods

BEST	Spectrophotometric - precision: 0.002, accuracy: 0.004
ACCEPTABLE	Potentiometric – precision: 0.002, much less stable and accurate; significant requirements for high-quality data

Sampling and analytical considerations

- Report standards, temperature, and pH scale (NBS, SWS, total hydrogen) in metadata
- Temperature control critical for pH measurements; should always report temperature at which pH was measured (usually 25°C)
- It is essential that samples be handled so as to minimize any CO_2 exchange with the atmosphere

- See detailed analytical guidelines for spectrophotometric pH determination in Section 2.3.4, including notes about the use of purified dyes when possible - e.g., high-purity crystallized indicators (R. Byrne, USF) provide milli-pH sensitivity

Emerging technology

- Ion-sensitive field effect transistor (ISFET) – e.g., DURAFET, milli-pH sensitivity (though still lacking a good seawater calibration protocol)

2.7.5. Computations

Ranking of available methods

Given sufficient information about the carbonate system in seawater, which typically includes **two measured CO_2 parameters**, salinity, temperature, boron/salinity ratio, and 5 equilibrium constants (K_0, K_1, K_2, K_B, K_W) appropriate to the desired temperature and pressure, one can calculate the composition of the seawater (with respect to these acid-base species). Note that one might also need the calcium/salinity ratio and the appropriate solubility products for aragonite and calcite. In addition, if there are other acid-base systems present in non-negligible amounts (*e.g.*, phosphate or silicate), then their total concentrations and appropriate equilibrium constants are needed too. Each of these terms has an uncertainty associated with it, and thus any calculated values will have an uncertainty that must be estimated by normal error propagation methods.

For any user, the combination of measured vs. calculated CO_2 parameters depends on: 1) what they want to know; 2) the measurement uncertainty they require, and; 3) how achievable that uncertainty is given their analytical resources. The possible combinations in order of increasing achievable uncertainty are as follows:

BEST	Measure one state (DIC or TA) and one quasi-state (pCO_2 or pH) variable
GOOD	Measure two state (DIC and TA) variables
ACCEPTABLE	Measure two quasi-state (pCO_2 and pH) variables

Recommendations

- Need to compare computations of seawater carbonate chemistry from different software packages (CO2SYS, CO2CALC, R-based, etc.); IOCCP currently funding such an intercomparison exercise
- Need to make uncertainty propagation calculations straightforward for the typical user
- Need better quantification of equilibrium thermodynamics and dissociation constants outside typical range of temperature and salinity (e.g., < 0°C and salinity close to 0)
- Need community consensus on how to estimate uncertainty for the various sample-specific measurements that will be appropriately implementation-specific
- Need community consensus on the appropriate uncertainties for the manifold data on equilibrium constants, etc. that are used in these calculations

2.8. RATES

Introduction

Working group members: M. Lomas (lead), V. Lutz (lead), C. Chandler, M. Church, R. Goericke, D. Grundle, M. Kampel, D. Kim, J. Ledesma

This working group focused on methodologies for rate measurements of primary (phytoplankton) and bacterial production. The most common method used to measure primary production is the tracer incubation, which varies among time-series in format (e.g., in situ vs. deck incubation), incubation time (e.g., dawn/dusk, full 24 hours, short period around local noon), and tracer (e.g., ^{14}C, ^{13}C) used. Mass of carbon per unit volume per day is the reporting unit for primary production. Bacterial production incubations are typically conducted with the radioactive tracers thymidine and leucine. Bacterial production is generally reported in pmol of substrate taken up, which is then converted to carbon using empirically determined or pre-defined constants.

Overall recommendations

- Most time-series have on-station time constraints that determine incubation period, so many carry out short incubations and multiply the results by a scaling factor to obtain a daily production rate; if possible, individual time-series should conduct routine dawn-to-dawn incubations (in situ is optimal, but on-deck is acceptable) alongside shorter incubations throughout the year (spanning different seasons); this will help assess the quality of scaled estimates and provide a common benchmark for comparison among time-series sites
- If a time-series has the facilities to analyze their own radioisotope or stable isotope samples, a replicate subset should routinely be sent to a centralized analytical facility (e.g., NASA pigment lab) to assess data quality (i.e. analytical accuracy)

2.8.1. Primary Production

Ranking of available methods

BEST	24-hour in situ incubation, dawn/dawn; use GF/F filters and replicate light bottles; at least one dark bottle should be included
GOOD	24-hour simulated[2] in situ incubation, dawn/dawn; use GF/F filters and replicate light bottles; at least one dark bottle should be included ~12-14-hour in situ/simulated in situ, dawn/dusk incubation; use GF/F filters and replicate light bottles; at least one dark bottle should be included
ACCEPTABLE	Fractional day incubations scaled to daily rates using experimentally determined conversions; use GF/F filters and replicate light bottles; at least one dark bottle should be included

[2]Simulated: deckboard incubation where bottles are screened to the light level from which they were collected.

Sampling and analytical considerations

- For short, several-hour incubations, daily integrated irradiance and irradiance during the period of incubation should be reported as part of the primary production data, as this is needed to convert short incubation rates to daily production rates, and can be useful for data interpretation
- For very short (~1h) Photosynthetron incubations, which measure physiological photosynthesis rates (i.e. PE curves), additional information on specific light levels in the Photosynthetron, as well as external light conditions, needs to be reported
- A uniform euphotic zone integration depth (e.g., 0.1% light level) should be defined; currently, most time-series use a fixed sampling integration depth
- For ^{14}C incubations, a bottle size of 250 mL is adequate; for ^{13}C incubations, the necessary volume will be larger, depending on the particulate biomass levels at the sampling site
- During primary production incubations, some fraction of the added isotopic label will end up in the dissolved organic carbon (DOC) pool. While GF/F filters are the preferred filter choice, it is important to note that GF/F filters may adsorb some $DO^{14}C$ produced during the incubation, thus leading to a potential overestimate of the 'particulate' primary production rate measurement. Even if the methods for estimating $DO^{14}C$ production are difficult and have a relatively large error due to subtraction of the 'particulate' OC from the total OC, it is still recommended that $DO^{14}C$ production be assessed independently (Karl et al., 1998) to account for the fraction of primary production released in the dissolved phase.
- Cleanliness and caution are always advised when making these measurements; cleaning protocols should periodically be revisited to ensure data quality
- Due to potential constraints on the acquisition of ^{14}C, many time-series are making primary production measurements with ^{13}C. Limited data suggest that primary production incubations done with ^{14}C vs. ^{13}C are comparable, but time-series should perform their own internal comparisons of the two tracers; all protocol changes need to be well documented in the metadata
- There are other methods that provide production-related parameters, such as triple oxygen isotopes (can provide gross and net primary production), bulk dissolved oxygen changes (net community production), and dilution experiments (estimate of phytoplankton growth rate, which can be converted to primary production with some assumptions). However, these methods *indirectly* measure primary production (i.e. direct fixation of carbon), and should be compared to *direct* primary production methods with caution

Available standards

As a rate process, there is no analytical standard. Careful and consistent technique, confirmation of specific activity in tracer stocks, and validation of assumptions are needed to ensure high-quality data.

Emerging technology

- There are emerging technologies (e.g., see FRRF below) that can indirectly measure primary production (or related parameters such as net community production); it is recommended that validation of these new methods be continued to determine how they compare to tracer incubations
- FRRF (Fast Repetition Rate Fluorometry): Measures in vivo fluorescence of phytoplankton by using a series of fast repetition rate excitation flashes and records resultant changes in fluorescence yield of

Photosystem II. Certain assumptions are then made as to how this translates to carbon fixation. This is not an incubation-dependent method; tracer incubations directly measure what happens after the sample is collected and during the incubation. Rather, FRRF reflects the condition of the system at the time of measurement. This technology has high potential due to its non-destructive nature and rapid analysis, but needs further calibration and assessment relative to the tracer methods. Furthermore, this technique is highly dependent on the phytoplankton species in the samples, since it measures the variable fluorescence in Photosystem II, and different algae have different arrangements of photosystems (Lutz et al., 2001; Suggett et al., 2004; Johnsen and Sakshaug, 2007). Subsequently, the sequence of flashes may have to be adjusted for resident phytoplankton assemblages and/or different types of oceanic waters.

2.8.2. Bacterial production

Ranking of available methods

BEST	1-6 hours in situ dark incubation with radioactive tracers (leucine and thymidine) is sensitive method
GOOD	Lab incubations with radioactive tracers such as 3H- Leucine, 3H- Thymidine, 3H-adenine
ACCEPTABLE	Immunochemical assay using non-radioactive BrdU as a proxy for Thymidine incorporation

Sampling and analytical considerations

- Separate incubations using leucine and thymidine tracers are recommended; these tracers measure bacterial protein and DNA production, respectively, and thus provide different 'views' of bacterial production
- Time-series should empirically determine the appropriate concentration of precursor substrate (leucine or thymidine) suitable to saturate de novo synthesis pathways
- In order to fully understand the rate measurement being made, the uptake kinetics of the chosen substrate should be measured to ensure that the amount added is saturating; the linearity of uptake over the course of the chosen incubation duration must be measured
- Short (~4-hour) incubations are preferred, but comparisons with longer (e.g., 12-24-hour) incubations are encouraged
- Incubations, if not done in situ, need to be done at temperatures similar to in situ temperatures; in addition, the role of water pressure should be considered, although this is difficult to address in on-deck incubations
- Unlike primary production, for which measurements are made in carbon units, estimates of bacterial production using thymidine or leucine incorporation still require conversion factors to get values into carbon or cellular production rates

Available standards

None

Emerging technology

- Immunochemistry merged with flow cytometry is a promising emerging technology; however, sensitivity and repeatability is still problematic for oligotrophic samples

2.9. TRAP FLUXES

Introduction

Working group members: M. Conte (lead), R. Lampitt (lead), M. Honda, R. Johnson, R. Letelier, J. Olafsson, M. Telszewski, K. Björkman

The group discussion was limited to fluxes measured by drifting traps (surface tethered and neutrally-buoyant traps) and moored traps only. We reviewed and revisited protocols published in JGOFS (1994) and SCOR (2007) reports. The group recognized and acknowledged the unresolved questions regarding hydrodynamic influences on trapping efficiencies. However, despite potential artifacts, the group noted that there is remarkable internal data consistency within studies (e.g., moored trap fluxes at different depths – e.g., CARIACO comparisons using PITS to assess flux within vs. to the bottom of the euphotic zone) and also in intercomparison of different trapping methods at a single site (e.g., BATS drifting vs. NBST comparisons; BATS drifting vs. OFP deep moored fluxes). This consistency lends confidence in flux quantification, despite known caveats in trapping methodologies.

2.9.1. Collection methods

This working group discussed two different types of traps, but did not rank them:

Drifting surface-tethered traps and neutrally buoyant sediment traps (NBSTs)

The group noted that in both tethered and neutrally buoyant traps, there is high variability in the amount of flux material collected in different tubes in the same deployment. A major question of the group was the reason(s) for this variability.

Sampling and analytical considerations

- Use multiple tubes/measurement (if possible, develop methods to combine tubes and then quantitatively split to reduce measurement uncertainty)
- Use blank tubes
- Preservative
    - 5% buffered formalin is typically recommended for standard open ocean measurements; however, the group noted that there have not been any quantitative studies published with exception of Lee et al. (1992) to determine optimal preservatives/poisons and concentrations thereof; brine strength also varies among different time-series, and the optimal brine strength has not been resolved
    - 8-10% formalin, buffered with combusted Na-borate to pH of ~8.0 is recommended in conditions with abundant swimmers and high POC fluxes (water depths <500 m, deployments >6-10 months, etc.), as 5% buffered formalin is largely incorporated into the swimmer tissue, leaving too little of the poison to prevent POC degradation
    - To avoid POC degradation due to binding of poison to organic material, S. Manganini and C. Pilskaln (Pers. comm.) have devised a small poison dispenser (very fine, plastic Nitex mesh containing a high density 8-10% formalin solution) that is placed in the bottom of 500-ml trap cups prior to emplacement on the trap carousel, which allows for slow dispersion of formalin over longer deployments and/or when swimmers and POC input to cups is elevated

Moored traps

The group recognized the greater problems with trapping at mesopelagic depths (200-1,000 m) for three reasons: (1) higher swimmer contamination, (2) stronger currents in this depth range potentially introduce larger hydrodynamic biases and uncertainties in trapping efficiency, and (3) the potential for degradation of flux composition during the collection period. Auto-oxidation artifacts have been poorly characterized.

Sampling and analytical considerations

- Deploy on subsurface moorings to reduce hydrodynamic influences
- Deploy current meters and tilt and pressure sensors to gain information about trapping environment and potential hydrodynamic biases on the fluxes
- Preservatives: Brines with addition of ~5% buffered formalin or $HgCl_2$ (200mg/l, Lee et al., 1992) appear to be comparable (lipid comparison)

2.9.2. Sample processing

The group discussion focused on sample processing methods and three main artifacts that affect accuracy of flux determinations: dissolution, lack of quantitative sample splitting, and swimmer removal.

Dissolution into the supernatant

Most moored trapping programs do not quantitatively measure losses into the dissolved phase and thus there are unknown errors in flux determinations; this is especially acute for some elements.

Sampling and analytical considerations

- For moored traps, measure salinity and pH
- Retain supernatant for analyses of dissolved species (see Section 2.10.2)
- Measure both particulate and dissolved phases when possible (esp. P, C, N)

Quantitative sample splitting

Moored traps (and conical NBSTs) generally split samples using a McLane splitter or similar (~3-5% error). The group recommends splitting of the <1-mm size fraction only as there is a high error associated with quantitative splitting of >1-mm aggregates. If necessary to split the >1-mm fraction, this may require disaggregation prior to splitting.

Cylindrical traps (drifting) rarely collect enough material for splitting, usually dedicated tubes are used for analyses. However, due to the high variability among tubes, multiple tubes should be analyzed. If this is not practical, a better option to may be to combine tubes and then quantitatively split the material to reduce operational error.

Sampling and analytical considerations

- Programs should quantify splitting errors using typical flux materials

Swimmer removal

Swimmers are particularly problematic in drifting tethered traps, and in some environments, in moored traps at mesopelagic depths. Both screening and handpicking are acceptable methods used by time-series for swimmer removal, but each method has its limitations. Screening is more consistent, but can result in the loss of larger size fractions (i.e. aggregates), and furthermore fails to remove swimmers smaller than the sieve size, which can have an appreciable mass. Picking is more time-consuming and subjective, and can still result in loss of fine particles that adhere to swimmers. The group noted that flux material is much easier to accurately pick without loss of fine particles when it is first screened through sieves to remove the finest size fractions.

Sampling and analytical considerations

- When possible, employ screening followed by hand-picking of swimmers under a dissecting microscope

2.9.3. Data reporting

The group noted that interpretation of flux results is aided by reporting in publications information about the sampling environment and noting any collection periods where the PI has concerns over the accuracy of the measured flux magnitude or flux composition for various reasons (e.g. high swimmer contamination, extreme currents, etc.).

Reporting considerations

- Measure and report data on trapping environment (currents, pressure, tilts, etc)
- Report variance among tubes, splitting errors
- Identify anomalous collection periods (e.g., extreme occurrences), flag data where flux and/or compositional data may be questionable (e.g., swimmer contamination, extreme currents)

2.9.4. Proposed studies to better understand and reduce trapping uncertainties

The group noted that despite some progress, many questions related to trapping efficiency and potential collection artifacts that have been posed in earlier reports remain largely unresolved.

Recommendations

- More replicated deployments of drifting trap and NBST arrays are needed to gain better understand of trapping uncertainties and small-scale spatial variability
- Targeted experiments using instrumented moored traps to obtain hydrodynamic data are needed to study the effect of environment and differences in trap geometries on trapping efficiency
- Revisit methods and deterrent approaches to minimize swimmer contamination during collection in order to improve flux data quality at mesopelagic depths
- Studies are needed to assess potential biases in flux measurements arising from the perturbation of natural environment by the trap surfaces (e.g., traps as attractant for macrozooplankton and fishes, growth of microbes on trap surfaces)

- Recommend collation of data from previous studies on the effects of different preservatives/poisons on maintaining sample integrity during deployment, potential artifacts of different methods, etc.
- Targeted experiments using moored traps are needed to assess material alteration during the collection period under different preservative/poison regimes

2.10. ORGANIC MATTER

Introduction

Working group members: C. Carlson (lead), L. Lorenzoni (lead), M. Blum, M. Cañon Paez, M. Erickson, O. Kawka, J. Rojas, F. Tapia, L. Valdes

This working group focused on methodologies for both dissolved (DOC/DON/DOP) and particulate (POC/PN/POP) organic matter.

Overall recommendations

- Glass fiber filters (GF/F) for both DOC and POC/PN should be combusted for 4-5 hours at 425-450°C (check furnace temperature prior to combustion) to remove organics associated with the filter matrix; higher temperatures may compromise the integrity of the filter
- Precombusted filters should be kept in small aluminum foil packets (~25 filters per packet) to reduce contamination on the ship

2.10.1. Particulate organic matter

Ranking of available methods

POC/PN

BEST	High Temperature Combustion via Elemental Analyzer (EA). Run total C (via EA) and PIC (coulometrically) directly to assess POC by difference
GOOD	High Temperature Combustion via Elemental Analyzer (EA). Acidify (fume) the filters prior to the run to eliminate existing PIC

Particulate Phosphorous (PPhos)

BEST	Ash Hydrolysis

Sampling and analytical considerations

- Reporting filtration volume is critical; volume may vary between sampling sites due to different oceanographic conditions
- Special attention should be paid to filtration volume in order to avoid filter overloading, and filtration rate should be kept low to avoid rupturing particles and forcing them through the filter
- POC/PN filters should dry for 24 hours at 60°C (monitor oven temperature during drying process); higher temperatures (>70°C) can result in N loss

- At least 3 blank filters should be kept and treated as "travel blanks" for blank correction of POC/PN
- Through high-temperature combustion, the result is likely to be total particulate carbon (POC+PIC); at some sites, the PIC contribution is minimal, thus the high temperature combustion of the untreated filter is essentially equivalent to POC; these methodological details should be reported in the metadata
- Ash hydrolysis is the best approach for measuring particulate phosphorous but this value includes both organic and inorganic phosphorous; also adsorption of DOP to GF/F filter can lead to overestimation of PPhos
- Empty the rosette sampling bottle contents into a separate carboy that can be mixed and further sampled to avoid bias against rapidly sinking particles (refer to Chapter 1 on sampling order for further information/recommendations on sinking particles); alternatively, the rosette sampling bottle can be directly subsampled, which is more acceptable in oligotrophic systems
- Filtration should be set to low vacuum (5 in Hg), or positive pressure filtration
- Site-specific standards should be swapped amongst time-series for intercalibration
- Some time-series use pre-screening meshes to remove large particles (mainly swimmers) from the samples; these methodological details should be reported in the metadata
- Labry et al. (In press, Cont. Shelf. Res.) examined different methods for TPP, POP, and PIP determination in suspended particulate matter, and specifically utilized persulfate oxidation for POP determination. This is a newer method and further comparisons between persulfate oxidation and ash hydrolysis are needed

Available standards

- There are a variety of commercial standards available for POC/PN analyses (e.g. spinach or apple leaves) that can be used for sample processing
- Each site should also prepare their own “in-house” reference material representative of their local system, and these standards should be run multiple times in each EA run

2.10.2. Dissolved Organic Matter

Ranking of available methods

DOC or TOC

BEST	High Temperature Combustion (HTC)
GOOD	Persulfate Oxidation
ACCEPTABLE	UV oxidation

TDN

BEST	High Temperature Combustion (HTC); this method yields TDN, and the dissolved inorganic nitrogen (DIN) must be subtracted out, which can cause problems when NO_3 is too high (due to error propagation)
GOOD	Persulfate Oxidation – N blank issues can be resolved by recrystallizing the persulfate
ACCEPTABLE	UV Oxidation - yields more variable results; can result in loss of energetically important wavelengths

DOP

BEST	Persulfate Oxidation
ACCEPTABLE	UV Oxidation – this method can have problems with Si interference

Sampling and analytical considerations

- Nitrile or polyethylene gloves are acceptable
- Tygon tubing should be avoided, as it has a tendency to leach organics; silicone tubing is recommended
- For storage, samples should either be frozen upright at -20°C or acidified to pH 3 and refrigerated
- Glass vials are the preferred containers for DOC if you do not have to ship your samples; acid-washed HDPE bottles are an acceptable alternative container if the samples have to be shipped for analysis
- Filtering is recommended in coastal systems with high POC load, but handling increases the potential for contamination, so in oligotrophic or deep water systems where POM load is small, the collection of total organic matter (TOM) may be appropriate (> 97% is operationally defined as DOM)
- Filtration directly from the rosette sampling bottle (through combusted GF/F filters housed in polycarbonate in-line filters) into sample bottle is recommended to minimize sample handling and contamination
- In-house references should be analyzed with every run to assess analytical performance, and swapped amongst time-series for intercalibration purposes
- TDN methodological comparison notes
    - The HTC method is more automatic, requiring less manual handling than wet chemical methods (persulfate oxidation, UV), which may reduce potential for contamination.

- A methodological comparison study by Bronk et al. (2000) reported higher yields with high temperature combustion (HTC) and persulfate oxidation, whereas UV gave lower, more variable yields
- A community intercomparison study by Sharp et al. (2002) reported more comparable yields among the three methods, but highlighted the need for more procedural uniformity among laboratories and the importance of quantifying DIN measurement variability
- HTC instrumentation comparison study for TDN analysis was conducted by Sharp et al. (2004)

Available standards

There are no certified reference materials for DOM. The Hansell Consensus Reference Material (CRM) provides a means of intercomparison across different sites. The following is recommended for site-specific standards:

- It is recommended that laboratory and storage freezer are dedicated volatile organic-free areas (i.e. samples should not be stored or analyzed in the presence of solvents, fixatives)
- Each time-series should have their own reference water; some time-series use deep water, which at some sites has a known, more stable concentration
- Make 2-3 large volume (8-10 L) in-house references that are calibrated against the Hansell CRM every 2-3 months
- These in-house references, along with blank water, should be run every 8- 10 samples to assess performance of the analytical run
- References should not vary by >2–3% over the course of an acceptable run
- When introducing new in-house references, the analysts should overlap reference batches for consistency

CHAPTER 3: RECOMMENDATIONS FOR FUTURE WORK

The issues of reproducibility, metrological traceability, and overall measurement uncertainty (Ellison and Williams, 2012) are paramount to ensuring intercomparability of time-series data sets. Participants recommended that time-series should leverage autonomous platforms when possible for internal calibration and method development and testing, though this does not necessarily provide a viable substitute for traditional biogeochemical and ecological measurements.

3.1. INTERNAL CONSISTENCY

In the interest of improving internal consistency within individual time-series and thus a common framework for comparison, workshop participants devised several simple, low-cost experiments that could be performed at time-series sites to assess the efficacy of current sampling and analytical protocols. Below are specific recommendations for the improvement of internal consistency within time-series:

1. Timing of particle sample draws relative to other variables, particularly in highly productive regions where particle settling in rosette sampling bottles post-collection could introduce a bias, is of concern (refer also to Section 2.1). Participants recommended dedicated rosette casts at least twice a year under different conditions (upwelling vs. non-upwelling, prevalence of different organisms, etc. – Gundersen et al., 2001), with repeat particulate sampling at regular time intervals to quantify the impact of particle settling and revisit sample extraction order if necessary.

2. Participants discussed the efficacy of different chlorophyll extraction techniques and solvents, including acetone, methanol, and dimethyl sulfoxide (DMSO), which can vary considerably, depending on local phytoplankton composition. They specifically recommended that time-series sites perform an experiment extracting Chl *a* with various solvents (DMSO, 100% acetone, methanol, etc.) and different extraction procedures (grinding, cold passive extraction, agitated extraction, etc.) in order to compare and document extraction yields. This experiment should be done on several occasions to capture any variability associated with seasonal changes in phytoplankton composition. Similar comparisons have been conducted (Wright et al., 1997; Latasa and Bidigare, 1998; Lutz et al., 2010) that could serve as a benchmark for time-series sites to pursue updated comparisons.

3. Rate measurements, such as primary production, typically involve in situ or simulated in situ ^{14}C or ^{13}C tracer incubation experiments. Time-series representatives reported a range of incubation time periods and conditions, depending largely on ship time constraints. Incubations that are less than 24 hours require that the measurements be scaled up to provide a daily rate. Given the lack of an analytical "standard" for this measurement and the end goal of data intercomparability, the rates working group identified an optimal method that involves a 24-hour dawn-to-dawn in situ incubation, with a dark bottle incubation and GF/F filters (see Section 2.8.1). Participants recommended that, if possible, time-series conduct an experiment in which they measure primary productivity using both their method and the optimal method to assess how their method compares and apply corrections if necessary. This type of comparison exercise conducted within time-series would help quantify the impacts of scaling and provide a common framework in which rate measurements can be compared across time-series. Some

time-series, particularly those in developing countries, use ^{13}C as a tracer due to the logistical difficulties of acquiring ^{14}C. To assess intercomparability between time-series using different isotopes, it is also recommended that time-series that have access to both isotopes compare rate measurements from incubations using the same method but different isotopes.

3.2. COMMUNITY INTERCOMPARISON

Intercomparison exercises serve many purposes, including method improvement and standardization, testing of new methods and emerging technology, and improving data inter-comparability across time-series. Plenary and working group participants highlighted ongoing activities such as the IOCCP-funded comparison of computational programs (CO2SYS, CO2CALC, R-based) used to calculate seawater CO_2 system parameters (J. Orr and J-P. Gattuso, lead PIs). They also suggested new intercomparison studies and external evaluation exercises that could be conducted across time-series to improve the quality and comparability of biogeochemical measurements:

- Flow cytometry cell count comparisons
- Nutrient intercomparison activity utilizing both commercially available primary nutrient standards and secondary internally calibrated standards
- Data comparison exercises across a suite of older vs. newer coulometric and infrared-based detectors being used to measure dissolved inorganic carbon (Section 2.7.1)
- Intercomparison exercise using ^{13}C as a tracer for primary productivity incubations
- Analysis of duplicate biogeochemical samples (nutrients, carbon, etc.) at select centralized facilities to assess internal analytical performance and provide a common framework for comparison
- Community-wide testing of less toxic poisoning approaches for ocean carbon measurements to eliminate the need for toxic mercuric chloride ($HgCl_2$; ongoing IOCCP Initiative)

Participants also discussed the importance of time-series as platforms for monitoring ocean acidification via the measurement of ocean carbon parameters pH, TA, DIC, and pCO_2. This requires that ocean carbon measurements performed at different time-series be evaluated against a common benchmark and that the different techniques be standardized to the degree possible. Such an activity might warrant its own focused workshop, as well as a series of community intercomparison activities as highlighted above. Ocean acidification is a time-sensitive issue, so those time-series that are not already making ocean carbon measurements might consider adding them to their current suite of measurements, as this could represent new sources of funding. IOCCP and OCB are heavily involved in developing a global ocean acidification monitoring network; those participating time-series that are making relevant measurements were encouraged to add their time-series information to this developing network.

3.3. METADATA DOCUMENTATION

The importance of detailed and carefully documented metadata cannot be overstated, as indicated by Church et al. (2013)**:** *"Detecting time-varying trends in ocean properties and processes requires consistent, high-quality measurements. Time-series must carefully document analytical procedures and, where possible, trace the accuracy of analyses to certified standards and internal reference materials."* While many of the methods being used today are based on long-established JGOFS protocols, most

time-series have made adaptations based on local oceanographic conditions and logistical constraints. Some of these changes can strongly impact data intercomparability and, subsequently, the capacity to measure global trends. Although measurements are made by different groups and at different times and places, it should be practical to consider them as a coherent dataset. Therefore, detailed methodological information, particularly accuracy and precision and how they are routinely determined and achieved, must be reported as part of the metadata.

Many sites also have a long history of testing their methods for efficacy and improvement, and have documented the results of such tests in data reports and other formats. This kind of information can provide observation-based justification for methodological adaptations, as opposed to decisions that may be perceived as arbitrary or anecdotal. Prior to the workshop, participants were asked to provide information on the biogeochemical parameters they measure and the associated methods they use to make the measurements. Based on metadata requirements raised in working group and plenary discussions during the workshop, participants were asked to provide more in-depth methodological information (see *time-series-at-a-glance* spreadsheet, Chapter 4) about their time-series. They have also provided links to documented analytical procedures when available.

3.4. AN INTERNATIONAL TIME-SERIES NETWORK

Workshop participants agreed that an international network of shipboard biogeochemical time-series would represent an effective initial step toward facilitating data intercomparability across time-series with the aim of improving our monitoring of global ocean change. This workshop and the time-series activities that preceded it (Chapter 1) have convened a growing body of scientific and analytical expertise, and helped establish a preliminary framework for such a global network. This network will not be limited to the participants of the workshop. Rather, workshop organizers and participants will continue to reach out to those time-series not represented at the workshop to include as many shipboard biogeochemical time-series as are interested in participating. Building on the materials from the workshop, this network will have a dedicated web presence (http://www.whoi.edu/website/TS-network/) and email list-serve moderated by the workshop organizers, and will facilitate enhanced coordination and communication among time-series, including information and data exchange, networking (training and job opportunities), capacity-building, and calibration and intercomparison activities. Participating time-series will include information about the parameters they measure and the methods they use, including detailed metadata, to help data users make informed choices when comparing data from multiple time-series. To support this network, the workshop fostered an atmosphere of data sharing and open-data policies. When possible, participating time-series should provide direct links or contacts for data access.

3.5. HIGH-PRIORITY MEASUREMENTS FOR MONITORING GLOBAL CHANGE

Biogeochemical time-series generate observations required to monitor the chemistry and ecology of the ocean. To gain meaningful information about global ocean variability and ecosystem function, time-series must collect a 'minimum' set of core measurements; such measurements are critical for intercomparison among sites, and their collection at multiple sites across all ocean basins is needed to characterize large-scale patterns and provide a global perspective of ocean change. This 'minimum' set of core measurements should comprise basic, easy-to-measure (not too costly, not requiring state-of-

the-art instrumentation) parameters that will enable us to address fundamental questions relevant to ocean change. These observations represent the building blocks of a truly inclusive international network of biogeochemical ocean time-series, which is an essential component of global ocean observing.

3.5.1. Core Biogeochemical Parameters

The 'minimum' set of core observations listed below should form the basis of any biogeochemical time-series. Optimally, these measurements should be collected at a temporal frequency that can resolve the seasonal cycle of the system, but it is recognized that this is logistically impossible for many time-series. We also recommend that time-series be established with the intent of being sustained for a prolonged period of time (decades). Long-term data sets generated by ocean time-series provide a valuable baseline of marine ecosystem and biogeochemical variability that allows us to place contemporary ocean changes in a broader temporal context.

We recommend that the 'minimum' set of core variables required to maintain an ocean biogeochemical time-series includes **temperature**, **salinity** and **chlorophyll a (Chl *a*)**, measured at least at the surface. Temperature and salinity provide the most basic information on physical water properties, and when measured throughout the water column, yield insight into local water masses and mixing processes. They are also essential to understanding key biological and biogeochemical processes, including marine ecosystem changes and fluctuations in the inorganic carbon system. Temperature and salinity measurements are straightforward to obtain via in situ sensors on a CTD, which can provide high vertical resolution and accuracy (Section 2.4). Chl *a* is the most commonly used proxy for phytoplankton biomass. It is an essential parameter for marine biogeochemical and ecosystem studies, as it provides fundamental information on marine phytoplankton distribution and interaction with local ocean biogeochemistry and physics. Chl *a* can be estimated in various ways, including in situ sensors (in vivo fluorescence; Sections 2.3.7 and 2.4) and through laboratory analysis (HPLC, spectrophotometry, fluorometry; Sections 2.2.1 and 2.6.4).

As resources allow, other important core measurements can be added to this minimum list. The next measurement that should be considered is **oxygen**, followed by **inorganic macronutrients**. Oxygen measurements can help characterize and quantify important processes related to ocean circulation, biogeochemical cycling, primary and net community production, etc. Oxygen time-series are also important for detecting trends in the world's oxygen minimum zones and associated marine food webs. Dissolved oxygen can be measured by in situ sensors (Sections 2.3.8 and 2.4) and laboratory analysis (Section 2.4). In situ oxygen sensors have undergone improvements resulting in more precise and stable measurements over extended periods of time, thus facilitating their deployment by both shipboard and autonomous time-series. Inorganic macronutrients are among the most fundamental of marine biogeochemical cycles, bearing inextricable links to marine biomass. When paired with biological and physical measurements, they provide information about the timing and magnitude of phytoplankton blooms and in some regions may regulate productivity. Some nutrients can be measured using in situ sensors (e.g., NO_3), but most nutrient measurements at biogeochemical time-series are currently done on discrete samples in the laboratory using a variety of wet chemistry and automated techniques (Section 2.5). These techniques generally require a trained level of expertise. While wet chemistry techniques are relatively easy to implement, substantial investment in equipment (e.g., Autoanalyzer) is required to conduct the automated measurements that can accommodate high sample throughput.

Key questions surrounding ocean and climate change often drive the research done at time-series. Indeed, some time-series may have been established to carry out specific research (e.g., following HABs events, evaluate implications for fisheries, following the response of the system to changes in local forcings such as upwellings, etc.). Depending on the scientific question of interest, additional measurements may be needed. Two current issues of global concern are ocean acidification and climate-driven marine ecosystem shifts. To address these questions, we recommend the following minimum suites of measurements to be added to the aforementioned core measurements.

3.5.2. Ocean Acidification

Understanding physical and biogeochemical controls on ocean CO_2 uptake and distribution, including both coastal and open ocean regions, is fundamental to the study of ocean acidification and its impacts on marine ecosystems and ocean health. Due in part to long-term ocean time-series (e.g., BATS - Bates, 2012; Bates et al., 2012; HOT - Doney et al., 2009), we are detecting local and regional trends in the inorganic carbon system that have implications for marine life, including changes in calcium carbonate saturation state. Ocean acidification will continue to impact marine food webs, including resources on which humans depend. Quantifying the inorganic carbon system requires measurement of at least **two inorganic carbon system variables** (pH, pCO_2, TA, DIC; see detailed recommendations in Section 2.7), along with temperature, salinity and inorganic nutrients (specifically phosphate and silicate). While these are the suggested minimum list of variables required to monitor ocean acidification, other variables such as dissolved oxygen should also be considered.

3.5.3. Marine Ecosystem Shifts

Many regions of the world's oceans are experiencing concurrent changes in temperature, pH, oxygen, nutrients, circulation, and stratification, which are affecting the health and structure of marine ecosystems, including changes in biogeographic distributions, species interactions, biodiversity, community structure, etc. (Doney et al., 2012). One of the fundamental observations needed to characterize and monitor marine ecosystems is **phytoplankton functional type**. Changes in phytoplankton community composition can be linked to processes that operate from the bottom up (e.g., changes in nutrient availability and other biogeochemical cycles that affect primary production) or from the top down (e.g., loss or gain of ecologically dominant predators). A routine and straightforward method for monitoring phytoplankton functional types is size-fractionated Chl *a* (Section 2.2). By filtering Chl *a* samples through filters of different pore sizes (e.g., 2-µm filter vs. 7-µm filter, which is the nominal GF/F pore size), it is possible to calculate, by difference, the Chl *a* contained in the different phytoplankton size fractions. Changes in the size structure can be obtained by looking at the ratio of large to small cells, which can provide information about shifts in the phytoplankton community. Another method is taxonomic assessments via microscopy (Section 2.6). While time consuming, microscopy provides information on micro- and nano-phytoplankton. It can be sufficient to develop an index for community structure baselines and to evaluate trends over time. Adding pigment analysis (HPLC; Section 2.2) and bio-optical observations can provide information on the contribution of each functional group to the total phytoplankton community.

3.6. FUNDING AND BUILDING CAPACITY

Time-series sites continue to face multiple challenges, particularly with regard to sustained long-term funding. In addition to amending their suite of parameters to include high-priority measurements with ample funding opportunities (e.g., ocean acidification, micro-plastics, etc.), time-series are encouraged to diversify their funding sources. Global economic challenges will likely continue to negatively impact government spending on science, but private sources (corporations, foundations, etc.) are becoming a much more prevalent scientific funding source.

The logistical challenges of maintaining time-series, particularly in developing countries, can pose significant obstacles to data quality and intercomparability. For example, the difficulties of acquiring ^{14}C to conduct primary productivity incubations has forced many time-series to move to ^{13}C as a tracer, which will require further testing and careful documentation before it can be considered a viable method that is comparable to ^{14}C-based rate measurements. Furthermore, many have difficulties accessing the necessary analytical facilities to run samples in-house and are forced to ship samples abroad, which can be costly and time-consuming. Factory calibrations of CTD and other seagoing instrumentation is a big issue for developing countries, since regulations make it difficult to ship these instruments abroad for testing. Workshop participants strongly considered these challenges in their working group discussions and methodological rankings (see Chapter 2 for more detailed parameter-specific recommendations). With the recognition that not all time-series have access to the more universally accepted protocols, instruments, and materials, participants identified several mechanisms for building capacity and improving data intercomparability:

- Time-series partnerships with local scientists and institutions to promote research collaborations and increase access to analytical facilities, instrumentation, autonomous sensors, etc.
- A move toward centralized analytical facilities for processing biogeochemical measurements (carbon, nutrients, etc.)
- Scientific products to increase visibility and demonstrate value of time-series to current and potential sponsors (e.g., ICES-type reports)
- Experiments conducted by multiple time-series to compare data generated via optimal vs. simpler, less costly methods
- A move toward less toxic and more easily accessible substances (e.g., ^{13}C vs. ^{14}C tracers in primary productivity incubations, alternatives to $HgCl_2$ for poisoning CO_2 samples and Cd for nitrate reduction, etc.)
- Expanded efforts to link scientists traveling between developed and developing countries to perform “calibrations of opportunity” on instrumentation

CHAPTER 4: WORKSHOP MATERIALS

4.1. AGENDA

Global Intercomparability in a Changing Ocean
An International Time-Series Methods Workshop

November 28-30, 2012 (Bermuda Institute of Ocean Sciences)

WORKSHOP AGENDA

Tuesday November 27, 2012

Participants arrive in Bermuda

Wednesday November 28, 2012

08:00-08:15 Bus transports participants from Grotto Bay Beach Resort to BIOS

08:15-09:00 Coffee and continental breakfast

09:00-09:15 **Welcome and introduction** (W. Curry & N. Bates, BIOS, H. Benway, OCB, M. Telszewski, IOCCP)

09:15-09:30 **Workshop objectives** (L. Lorenzoni, USF)

09:30-10:30 **Plenary talks** (20 minutes each):
Scientific importance of time-series: Repeat Hydrography (R. Wanninkhof, NOAA)
Scientific importance of time-series: Insights from fixed point observations (R. Lampitt, NOCS)
Challenges of maintaining/sustaining time-series in developing countries (V. Lutz, INIDEP)

10:30-11:00 Coffee break

11:00-11:30 **Time-series methods overview: Why results must be comparable from site to site** (K. Johnson, MBARI)

11:30-12:45 **Working Groups: Sampling protocols** *(each WG will have a list of time-series to examine* the order of discrete sample extraction*) - each chaired by a SAC member*

12:45-14:00 Lunch

14:00-14:20 **The Bermuda-Atlantic Time Series: An example of long-term time-series work** (M. Lomas, BATS/Bigelow)

14:20-17:00 **BATS tour**

17:00 **Poster session and mixer** (participants present a poster on their time-series)

19:00 Group Dinner at the Swizzle (http://www.swizzleinn.com)

Thursday November 29, 2012

08:00-08:15 Bus transports participants from Grotto Bay Beach Resort to BIOS

08:15-09:00 Coffee and continental breakfast

09:00-10:00 **Day 1: Sampling protocol working group reports (Moderator: L. Lorenzoni)**

10:00-11:00 **Working Groups - Discrete parameters, round I** *(each working group will have one variable assigned and will essentially build on the current core protocols)*

1. **Pigments**
2. **In line measurements**
3. **CTD parameters/discrete calibrations**
4. **Inorganic macro and micronutrients**
5. **Biomass**

Guiding questions for the working groups:

a. *How many different methods are being used to measure these parameters, and are they intercomparable (i.e. has there been a direct comparison of the various methods)?*
b. *Is there a consensus ranking of established methods (i.e. if you can't do X then proceed with Y)? If not, can we make one?*
c. *What steps can we take now to ensure standardization of the methods? If consensus standards or CRMS are not available how do we achieve a meaningful comparison?*
d. *Are there standard available? (same/different)?*
e. *What are the limitations of each method?*
f. *What are the uncertainties (QA/QC discussion)?*
g. *What are the various state of the art methods and are there emerging technology for measurements is available?*
h. *Is there a different nomenclature utilized at different time-series for these parameters? How can we standardize the nomenclature and reported units between time-series?*

11:00-11:30 Coffee break

11:30-12:30 **Working Groups - Discrete parameters, round I (continued)**

12:30-14:00 Lunch

14:00-16:00 **Working Groups - Discrete parameters, round** *(each working group will have one variable assigned and will essentially build on the current core protocols) – See guiding questions above*

1. **Carbonate System**
2. **Rates**
3. **Traps/Fluxes**
4. **Organic matter**

16:00-16:30 Coffee break

16:30-18:00 **Round 1 Discrete Parameters Working Group reports and open discussion** (Moderator: N. Bates)

18:00 Bus transports participants from BIOS to Grotto Inn

19:00 Group dinner/celebration at the Grotto Inn

Friday November 30, 2012

08:00-08:15 Bus transports participants from Grotto Inn to BIOS

08:15-09:00 Coffee and continental breakfast

09:00-10:30 **Round 2 Discrete Parameters Working Group reports** (working group leaders) **and open discussion** (Moderator: K. Johnson)

10:30-11:15 **Building consensus on biogeochemical sampling and measurement protocols** (plenary discussion moderated by L. Lorenzoni, H. Benway, M. Telszewski)
Guiding points for discussion include:

a. *identify major discrete sampling and measurement/analytical issues and define paths forward*
b. *Work on the base of a best practices guide (BPG) and modify it so that it describes the results from the working groups*
c. *BPG final categorization of methods will feature a tiered approach (with published precision and accuracy) so that methods are classified as:*
    i. *optimal = highest quality (accuracy/precision) and/or efficiency*
    ii. *good = medium quality (accuracy/precision) and/or efficiency*
    iii. *acceptable = lowest quality (accuracy/precision) and/or efficiency*

d. *Provide recommendations to facilitate comparison among TS that are using different protocols*
e. *What technologies are available to conduct the measurements identified? What is desired?*

11:15-11:30 Coffee break

11:30-12:30 **Building consensus on biogeochemical sampling and measurement protocols** (discussion cont'd)

12:30-14:00 Lunch

14:00-14:30 Plenary talk: **Autonomous observations in the context of ocean time-series sites: some recent science showcases** (A. Körtzinger)

14:30-15:00 Group discussion: **Recommendations for automated sensors/instrumentation (cross-calibration issues)** (Moderator: A. Körtzinger)

15:00-15:30 Plenary talk: **World of data: The joys of oceanographic time-series data** (C. Chandler)

15:30-16:00 Group discussion: **Cruise planning and metadata and building and/or improving infrastructure for data sharing** (Moderator: C. Chandler)

16:00 Adjourn

Participants can leave right after the workshop or stay until December 1. Your expenses will be covered for the night of November 30.

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APPENDIX 1. TIME-SERIES INFORMATION

PART 1. Time-series information (name, contact, coordinates, measurement duration and frequency, URL)

	REPRESENTATIVE	LOCATION	DURATION	FREQUENCY	METHODS INFORMATION	DATA ACCESS
SOUTH PACIFIC						
Munida	Kim Currie	Surface transect from 45.77°-45.84° S, 170.22°-171.54° E	1998-	6 cruises/yr		
IMARPE (Callao)	Jesús Ledesma	12.1° S - 77.2° W (Peru Shelf) and Transect 12.1 - 12.2 ° S - 77.1 - 78.0 °W	20 years	4cruises/yr	http://www.imarpe.pe/imarpe/index.php?id_seccion=I01080201000000000000	http://www.imarpe.pe/imarpe/index.php?id_seccion=I01380000000000000000
COPAS	Fabian Tapia	36.5° S; 73.1° W (Chile)	2002-	monthly-seasonal cruises		
Eastern Australia	Tom Trull	IMOS National Reference Station Network	variable, see pdf Long term sites: Maria: 1944-2005, Hacking: 1941-2004, Rottnest: 1951-2001	quarterly-monthly (varies by station)	http://imos.org.au/fileadmin/user_upload/shared/ANMN/IMOS_NRS_BIOGEOCHEMICAL_SAMPLIN/IMOS_NRS_BIOGEOCHEMICAL_OPERATIONS_PRACTICAL_HANDBOOK.v2.pdf	
NORTH PACIFIC						
Japan (JMA)	Masao Ishii, Yusuke Takatani	Transects along 137°E from 5-34°N and 165°E from 10-50°N	137°E transect: 1994- (1994-2002: irregular, 2003- : regular) 165°E transect: 2003-	137°E transect: 4 cruises/yr, 165°E transect: 2 cruises/yr		http://www.data.kishou.go.jp/kaiyou/db/vessel_obs/data-report/html/ship/ship_e.php
Japan (JAMSTEC)	Makio Honda	NW Pacific S1 (30°N, 145°E); K2 (47°N, 160°E), KNOT (44°N, 155°E)	S1: 2010-present; K2: 2001-present with some hiatuses; KNOT: 1997-present with hiatuses;	1-3 cruises/yr	http://www.jamstec.go.jp/rigc/e/ebcrp/mbcrt/index.html	
Ensenada	Eduardo Santamaria-del-Angel	31.2° N, 116.0° W (Mexico)	2007-	6 cruises/yr		
CalCOFI and CCE-LTER	Ralf Goericke	southern and central California	1949-	4 cruises/yr	http://calcofi.org/references/ccmethods, http://cce.lternet.edu/data/methods/	
MBARI	Marguerite Blum	Monterey Bay, CA	1989-	cruises ev. 2-3 weeks		
SPOT	Diane Kim	San Pedro Basin, CA	1998-	monthly cruises		
HOT	Karin Bjorkman, Matt Church	22.8° N, 158.0° W	1987-	10 cruises/yr	http://hahana.soest.hawaii.edu/hot/protocols/protocols.html	

	REPRESENTATIVE	LOCATION	DURATION	FREQUENCY	METHODS INFORMATION	DATA ACCESS
Line P	Kyle Simpson	SE/NW transect from 48.6° N, 125.5° W to 50° N, 145° W	1956-	2-3 cruises/year	http://www.pac.dfo-mpo.gc.ca/science/oceans/data-donnees/line-p/index-eng.htm#Presentsampling	
Station Papa	Adrienne Sutton	50°N, 145°W (P26 of Line P)	Mooring: 2007- Cruises: 1956-	2-3 cruises/yr (Line P, Fisheries and Oceans Canada) VOS cruises ev. other month Mooring: continous		
NEPTUNE Canada	Damian Grundle	NEPTUNE Canada Platform Array (5 instrumented sites along cabled observatory from west coast of Van Isle to regions beyond the continental slope)	2009-	2-3 cruises/yr	http://www.whoi.edu/fileserver.do?id=133464&pt=2&p=147790	
Santa Barbara Channel - Plumes and Blooms	Craig Carlson	NE/SW transect off Santa Barbara from 34.4°N, 119.8°W to 34.1°N, 120.0°W (7 stations)	1996-	monthly cruises		
CARIBBEAN SEA						
CARIACO	Jaimie Rojas, Laura Lorenzoni, Frank Muller-Karger	Venezuela (10.5° N, 64.7° W)	1995-	monthly cruises	http://www.imars.usf.edu/pubs/CARIACO_Methods_Manual.pdf	
Cartagena	Mary Luz Cañon Paez	Colombia (10.4° N, 76.0° W)	2008-	3 cruises/yr		
NORTH ATLANTIC						
Labrador Sea (BIO)	Stephen Punshon		1993-	1 cruise/yr		
Offshore Halifax Line	Stephen Punshon		2006-	1 cruise/yr		
Davis Strait	Stephen Punshon		2004-2011, 2013 and 2015 (planned)	1 cruise/yr		
Barrow Strait	Stephen Punshon		2003-2010 (2008 no data)	1 cruise/yr		
Hudson Bay and Strait	Stephen Punshon		2003-2006	1 cruise/yr		
PAP	Richard Lampitt	49.0° N, 16.5° W	1989-	Mooring		http://www.eurosites.info/pap/data.php
OWS M (Ocean Weather Station M)	Contacts: Ingunn Skjelvan and Truls Johannessen	66° N, 2° E (Norwegian Sea)	1948-2009	weekly-monthly (depending on variable)		

	REPRESENTATIVE	LOCATION	DURATION	FREQUENCY	METHODS INFORMATION	DATA ACCESS
ESTOC	Andres Cianca	29.2° N, 15.5° W	1994-	4 cruises/yr (since 2004)	http://www.estoc.es/en/images/stories/mediciones/MedicionesDiscretas_ESTOC_english.pdf	
A Coruña RADIALES (NW Spain)	Antonio Bode [antonio.bode@co.ieo.es]; M.T. Alvarez-Ossorio [maite.alvarez@co.ieo.es]	43.4 N -8.4 W western Iberian Shelf	1988- (zooplankton); 1989- (phytoplankton, CTD & nutrientes)	monthly cruises	http://www.st.nmfs.noaa.gov/nauplius/media/time-series/site__iberian-a-coruna-phy; http://www.st.nmfs.noaa.gov/nauplius/media/time-series/site__iberian-a-coruna. IEO core project: Studies on Time Series of Oceanographic data. In: Operational Oceanography: Implementation at the European and Regional Scales (N.C. Fleming et al.(ed.). Elsevier Science B.V., Amsterdam; ISBN 0-444-50391-9: 99-105	http://www.seriestemporales-ieo.com/en/resultados/datos.htm
Cape Verde Ocean Observatory - CVOO	Björn Fiedler, Arne Körtzinger	Eastern North Atlantic (17.6°N 24.3°W)	2006- (upgrades in 2013 - new testbed mooring, refit ship)	monthly cruises	not yet available - planned for 2013; Contact: Björn Fiedler	Meta-data publicly available; Measurement data restricted (login required). Web Portal (under development): https://portal.geomar.de/group/cvoo/home
BATS (inc. Hydrostation "S")	Rodney Johnson, Mike Lomas, Nicholas Bates	31.7° N, 64.2° W	BATS: October 1988- , HS: 1954-	15 cruises/yr	http://bats.bios.edu/bats_methods.html	
Irminger Sea	Jon Olafsson	64.33°N, 28.0°W	1983-	4 cruises/year	http://www.biogeosciences.net/6/2661/2009/bg-6-2661-2009.pdf	http://cdiac.ornl.gov/oceans/CARINA/
Iceland Sea	Jon Olafsson	68.0°N, 12.67°W	1983-	4 cruises/year	http://www.biogeosciences.net/6/2661/2009/bg-6-2661-2009.pdf	http://cdiac.ornl.gov/oceans/CARINA/
Oceanic Flux Program	Maureen Conte	31.7° N, 64.2° W	1978-	continuous (sediment trap)	See Conte, M.H. et al., 2001, Deep-Sea Res, Part II, 48, 1471--1505.	

	REPRESENTATIVE	LOCATION	DURATION	FREQUENCY	METHODS INFORMATION	DATA ACCESS
SOUTH ATLANTIC						
Ubatuba	Milton Kampel	23.5° S, 45.1° W (Brazil)	2004-	monthly cruises		
Epea	Ruben Negri/Vivian Lutz	38.5° S, 57.7° W (Argentina)	2000-	monthly cruises	Rubén Negri (negri@inidep.edu.ar)	Rubén Negri (negri@inidep.edu.ar)
SOUTHERN OCEAN						
Palmer LTER	Matthew Erickson	64.8° S, 64.1° W (Antarctica)	1990-	1 cruise/yr (10 ocean sampling sites around Palmer Station)	http://www.whoi.edu/fileserver.do?id=134184&pt=2&p=147869	http://oceaninformatics.ucsd.edu/datazoo/data/pallter/datasets
Southern Ocean Time-Series (SOTS)	Tom Trull	47ºS, 140ºE - 3 moorings (meteorology/oceanography, biogeochemistry, sediment trap) with annual servicing cruise	2007-	1 cruise/yr (mooring servicing)	http://www.whoi.edu/website/TS-workshop/imos.org.au/fileadmin/user.../IMOS_Factsheet_SOTS_web.pdf	
King Sejong Station (KOPRI)	Tae Siek Rhee	62.2° S, 58.8° W	1996* - (depending on parameters, the duration is different. In case of pCO2 of seawater, reliable data stard being logged in 2012)	every minute, every 5 minutes, or once a day depending on parameters		
INDIAN OCEAN						
Coastal Bay of Bengal (Vizag)	VVSS Sarma (sarmav@nio.org)	17.54° N, 83.52° E	2007-	monthly cruises		
Western Australia	Tom Trull (Tom.Trull@utas.edu.au)	IMOS National Reference Station Network	Maria: 1944-2005, Hacking: 1941-2004, Rottnest: 1951-2001	quarterly-monthly cruises (depending on station)	http://imos.org.au/fileadmin/user_upload/shared/ANMN/IMOS_NRS_BIOGEOCHEMICAL_SAMPLIN/IMOS_NRS_BIOGEOCHEMICAL_OPERATIONS_PRACTICAL_HANDBOOK.v2.pdf	

PART 2. Time-series measurements (sampling order, in-line measurements, pigments)

	SAMPLING ORDER	IN LINE MEASUREMENTS					PIGMENTS		
		Temperature	Conductivity (S)	pCO_2	Fluorescence (Chloropigment)	NOTES	Chl *a*	HPLC	NOTES
SOUTH PACIFIC									
Munida		SBE45/38	SBE45/38	IR			F(T)✠		
IMARPE (Callao)	O_2, N_2O, pH, DIC, Alk, Nutrients and Chla	SBE 56			WET Labs	C, T, P and D O. SBE 37 and SBE 63	F(T)✠	x	
COPAS							F		
Eastern Australia							F		
NORTH PACIFIC									
Japan (JMA)		SBE45	SBE4	IR	Turner		F		
Japan (JAMSTEC)		SBE43	SBE4	IR	Turner		F(T)	x	
Ensenada							F	x	
CalCOFI and CCE-LTER		Thermosalini-graph	Thermosalini-graph	Thermo-salini-graph	Thermosalinigraph		F✠	x	
MBARI		x	x	x	x		F	x	
SPOT							F		
HOT		x	x	x	x		F✠	x	
Line P							x	x	

	SAMPLING ORDER	IN LINE MEASUREMENTS					PIGMENTS		
		Temperature	Conductivity (S)	pCO_2	Fluorescence (Chloropigment)	NOTES	Chl *a*	HPLC	NOTES
Station Papa		x (mooring)	x (mooring)	x (mooring) also pH	x (mooring)		x	x	
NEPTUNE Canada		x	x		x		x		
Santa Barbara Channel - Plumes and Blooms							F	x	
CARIBBEAN SEA									
CARIACO	2 separate types of casts; Particle abs, taxonomy, Chla, HPLC; H2S, O2, pH, DOC/TOC, TA, nutrients, salinity						F(T)⌘	x	
Cartagena							S		
NORTH ATLANTIC									
Labrador Sea (BIO)	Transient Tracers, O2, TIC, TA, pH, d18O H2O, Salinity, Pigments, Nutrients	x	x		x		F	x	
Offshore Halifax Line	Transient Tracers, O2, TIC, TA, pH, d18O H2O, Salinity, Pigments, Nutrients	x	x		x		F	x	
Davis Strait	Transient Tracers, O2, TIC, TA, pH, d18O H2O, Salinity, Pigments, Nutrients	x	x						
Barrow Strait	Transient Tracers, O2, TIC, TA, pH, d18O H2O, Salinity, Pigments, Nutrients								
Hudson Bay and Strait	Transient Tracers, O2, TIC, TA, pH, d18O H2O, Salinity, Pigments, Nutrients								
PAP									

	SAMPLING ORDER	IN LINE MEASUREMENTS					PIGMENTS		
		Temperature	Conductivity (S)	pCO_2	Fluorescence (Chloropigment)	NOTES	Chl *a*	HPLC	NOTES
OWS M (Ocean Weather Station M)		SeaBird TSG	SeaBird TSG	shower head, IR detection			x		
ESTOC	O2, pH, Alk, DIC, Nutrients, Salinity, pigments	x (mooring)	x (mooring)	LICOR (mooring)	x (mooring)		F(T)✠	x	
A Coruña RADIALES (NW Spain)	O2, nutrients, pigments, POM, phyto, bacteria, zooplankton						F		
Cape Verde Ocean Observatory - CVOO	O2, DIC/TA, TOC, Nuts, POC, CHL	Microcat (mooring)	Microcat (mooring)	C (SAMI-2)		all measurements performed on a long-term mooring (being redeployed every 18 months); Incl. O2 measurements (Optode)	F		Chla solvent: Acetone
BATS (inc. Hydrostation "S")		x	x	LICOR	x		F✠	x	
Irminger Sea	O2, PCO2, pH, TCO2, Nutients, Salinity								
Iceland Sea	O2, PCO2, pH, TCO2, Nutients, Salinity								
Oceanic Flux Program									

	SAMPLING ORDER	IN LINE MEASUREMENTS					PIGMENTS		
		Temperature	Conductivity (S)	pCO_2	Fluorescence (Chloropigment)	NOTES	Chl *a*	HPLC	NOTES
SOUTH ATLANTIC									
Ubatuba		x	x		x		F		
Epea	Oxygen, Bacteria, CDOM, nutrients, chlorophyll-pigments, phytoplankton, salinity						F⌘		monthly frequency has many unfortunate gaps.
SOUTHERN OCEAN									
Palmer LTER		SBE38	SBE45	LDEO	ECO		F(T)✠	x	
Southern Ocean Time-Series (SOTS)		x	x	x	x		x		
King Sejong Station (KOPRI)		Thermocouple	x	IR	x		x		
INDIAN OCEAN									
Coastal Bay of Bengal (Vizag)							x	x	
Western Australia							x	x	

PART 3. Time-series measurements (CTD parameters and discrete calibrations)

	CTD PARAMETERS AND DISCRETE CALIBRATIONS								
	Depth (P)	**Temperature**	**Conductivity (S)**	**Dissolved Oxygen**	**Fluorescence (Chloropigment)**	**Beam Attenuation (c)**	**Dissolved Oxygen (discrete)**	**Salinity (discrete)**	**NOTES**
SOUTH PACIFIC									
Munida	SBE19	SBE19	SBE19						
IMARPE (Callao)	SBE19	SBE19	SBE19	SBE 43			W	GP	SBE 19 plus
COPAS	x	x	x	x	x		W		
Eastern Australia	x	x	x	x	x	x	W		
NORTH PACIFIC									
Japan (JMA)	SBE911	SBE3plus	SBE4	RINKO-III	Seapoint		W	GA	
Japan (JAMSTEC)	SBE9plus	SBE3	SBE4	SBE43/RINKO	Seapoint	C-Star	W	GA	
Ensenada	x	x	x	x	x				
CalCOFI and CCE-LTER	SBE911	SBE911	SBE911	SBE911	x	x	W	GP	
MBARI	x	x	x	x	x	x	W	GA	
SPOT	SBE911	SBE911	SBE911	SBE13	WETStar	AC3	W	GA	
HOT	x	SBE-3-02/F	SBE-4	SBE13	Sea-Tech flash fluorometer	x	W	M	
Line P	x	x	x	x	x	x	x	x	
Station Papa	SBE37/39	SBE37/39	SBE37/39	SBE43/Optode	ECO FLNTUSB	ECO FLNTUSB	x	x	
NEPTUNE Canada	x	x	x	x	x	x	W	x	
Santa Barbara Channel - Plumes and Blooms	x	x	x	x	x	x			

	CTD PARAMETERS AND DISCRETE CALIBRATIONS								
	Depth (P)	**Temperature**	**Conductivity (S)**	**Dissolved Oxygen**	**Fluorescence (Chloropigment)**	**Beam Attenuation (c)**	**Dissolved Oxygen (discrete)**	**Salinity (discrete)**	**NOTES**
CARIBBEAN SEA									
CARIACO	SBE29	SBE3	SBE4	SBE43	ECO Fluorometer	C-Star	W	GP	
Cartagena	x	x	x	x	x		W	x	
NORTH ATLANTIC									
Labrador Sea (BIO)									
Offshore Halifax Line									
Davis Strait									
Barrow Strait									
Hudson Bay and Strait									
PAP									
OWS M (Ocean Weather Station M)	SeaBird MicroCat (shipboard CTD and mooring)	SeaBird MicroCat (shipboard CTD and mooring)	SeaBird MicroCat (shipboard CTD and mooring)	mooring 2011- (Aanderaa Optode)			W	GP	
ESTOC	IDRONAUT OS316; Glider	IDRONAUT OS316; Glider	IDRONAUT OS316; Glider	IDRONAUT OS316; Glider	Glider slocum	Glider slocum	W	GA	Several CTDs (opportunity ships)
A Coruña RADIALES (NW Spain)	SBE25	SBE25	SBE25		x (various fluorometers)		W	GP	

	CTD PARAMETERS AND DISCRETE CALIBRATIONS								
	Depth (P)	**Temperature**	**Conductivity (S)**	**Dissolved Oxygen**	**Fluorescence (Chloropigment)**	**Beam Attenuation (c)**	**Dissolved Oxygen (discrete)**	**Salinity (discrete)**	**NOTES**
Cape Verde Ocean Observatory - CVOO	SBE 19plus	SBE 19plus	SBE 19plus	SBE 43	ECO FLNTURT		W	planned for 2013	
BATS (inc. Hydrostation "S")	SBE410K-023	SBE3	SBE4	SBE43	Chelsea	C-Star	W	GP	
Irminger Sea							W	GA	
Iceland Sea							W	GA	
Oceanic Flux Program	SBE410K-023	SBE3	SBE4	SBE43	Chelsea	C-Star			
SOUTH ATLANTIC									
Ubatuba	x	x	x	x	x	x	x	x	
Epea	x	x	x		Passive fluorescence Biospherical PUV		W	GA	
SOUTHERN OCEAN									
Palmer LTER	SBE9Plus	SBE3	SBE4	SBE43	ECO Fluorometer	C-Star	W		
Southern Ocean Time-Series (SOTS)	x	x	x	x	x	x			
King Sejong Station (KOPRI)	x	x	x		x	x			
INDIAN OCEAN									
Coastal Bay of Bengal (Vizag)	x	x	x	x	x		x	x	
Western Australia	x	x	x	x	x	x	x		

PART 4. Time-series measurements (inorganic macro- and micro-nutrients)

	INORGANIC MACRO- AND MICRONUTRIENTS									
	Nitrate + Nitrite	**Nitrite**	**Low Level Nitrate + Nitrite**	**Ammonium**	**Soluble Reactive Phosphorus (SRP)**	**Low Level SRP**	**Silicate**	**Biogenic (particulate) Si**	**Fe**	**NOTES**
SOUTH PACIFIC										
Munida	AA[2]				AA[2]		AA[2]			
IMARPE (Callao)	M	M			M		M			
COPAS	AA*			F	AA*		AA*			
Eastern Australia	x	x			x		x			
NORTH PACIFIC										
Japan (JMA)	AA	AA			AA		AA			
Japan (JAMSTEC)	AA*			AA*	AA*		AA*			
Ensenada	AA*			AA*	AA*		AA*			
CalCOFI and CCE-LTER	AA*			AA*	AA*		AA*			
MBARI	AA▼	AA▼		F	AA▼		AA▼			
SPOT	AA*			F	AA*		AA*	AA*		
HOT	AA*		Chemiluminescence		AA*	MAGIC	AA*	AA*	x	
Line P	x			x	x		x			
Station Papa	x			x	x		x			
NEPTUNE Canada	x			x			x			
Santa Barbara Channel - Plumes and Blooms	x				x		x	x		

	INORGANIC MACRO- AND MICRONUTRIENTS									
	Nitrate + Nitrite	**Nitrite**	**Low Level Nitrate + Nitrite**	**Ammonium**	**Soluble Reactive Phosphorus (SRP)**	**Low Level SRP**	**Silicate**	**Biogenic (particulate) Si**	**Fe**	**NOTES**
CARIBBEAN SEA										
CARIACO		AA*		AA*	AA*		AA*			
Cartagena	x	x		x			x			
NORTH ATLANTIC										
Labrador Sea (BIO)	AA*	AA*		AA*	AA*		AA*			
Offshore Halifax Line	AA*	AA*		AA*	AA*		AA*			
Davis Strait	AA*	AA*		AA*	AA*		AA*			
Barrow Strait	AA*	AA*		AA*	AA*		AA*			
Hudson Bay and Strait	AA*	AA*			AA*		AA*			
PAP										
OWS M (Ocean Weather Station M)	AA				AA		AA			
ESTOC	AA*				AA*		AA*			Quasimeme program for calibration
A Coruña RADIALES (NW Spain)	AA*	AA*		AA*	AA*		AA*			QUASIMEME (until 2006) & SCOR (2012) nutrient intercomparison exercises
Cape Verde Ocean Observatory - CVOO	AA*	AA*			AA*		AA*			Nitrate and nitrite are being reported separately; SRP Phosphate (no filtration) is being reported

	INORGANIC MACRO- AND MICRONUTRIENTS									
	Nitrate + Nitrite	**Nitrite**	**Low Level Nitrate + Nitrite**	**Ammonium**	**Soluble Reactive Phosphorus (SRP)**	**Low Level SRP**	**Silicate**	**Biogenic (particulate) Si**	**Fe**	**NOTES**
BATS (inc. Hydrostation "S")	AA▼	AA▼			AA▼	MAGIC	AA▼	x		
Irminger Sea	AA*				AA*		AA*			
Iceland Sea	AA*				AA*		AA*			
Oceanic Flux Program										
SOUTH ATLANTIC										
Ubatuba	x			x	x		x			
Epea	AA*	AA*			AA*		AA*			
SOUTHERN OCEAN										
Palmer LTER	AA**	AA** (only until 2008)		AA**	AA**		AA**			
Southern Ocean Time-Series (SOTS)	x				x		x			
King Sejong Station (KOPRI)										
INDIAN OCEAN										
Coastal Bay of Bengal (Vizag)	x			x			x			
Western Australia	x				x		x			

PART 5. Time-series measurements (biomass, rates)

	BIOMASS						RATES		
	Phytoplankton	**Microplankton**	**Zooplankton**	**Viruses**	**Bacteria & Cyanobacteria**	**NOTES**	**Primary Production**	**Bacterial Production**	**NOTES**
SOUTH PACIFIC									
Munida	F(T)✠								
IMARPE (Callao)	F(T)✠						14C		24 Hours
COPAS	F	M	DW		FC		O2/13C		
Eastern Australia	M		A				O2/gas sensor		
NORTH PACIFIC									
Japan (JMA)									
Japan (JAMSTEC)			NT		FC		13C	H3L	
Ensenada	F				EF		14C	H3L	
CalCOFI and CCE-LTER	F✠		NT		FC		14C		
MBARI		Slides			x		14C		
SPOT	F	FC/M		M	M			H3L	
HOT			x		FC		14C		
Line P			x						
Station Papa			x						
NEPTUNE Canada									
Santa Barbara Channel - Plumes and Blooms	F/M				FC				

	BIOMASS						RATES		
	Phytoplankton	**Microplankton**	**Zooplankton**	**Viruses**	**Bacteria & Cyanobacteria**	**NOTES**	**Primary Production**	**Bacterial Production**	**NOTES**
CARIBBEAN SEA									
CARIACO	F(T)⌘		NT/DW				14C	H3L	
Cartagena	S		NT/M						
NORTH ATLANTIC									
Labrador Sea (BIO)	F		x				x	x	
Offshore Halifax Line	F		x				x	x	
Davis Strait									
Barrow Strait									
Hudson Bay and Strait									
PAP									
OWS M (Ocean Weather Station M)			x						
ESTOC									
A Coruña RADIALES (NW Spain)	M, Lugol	NT/M/Vertical/40 µm mesh/Bongo	NT/DW/M/Obliq ue/ 200 µm mesh, Juday-Bogorov		FC (from 2003 onwards)		14C		Simulated 'in situ' 3 h (deck) incubation around noon
Cape Verde Ocean Observatory - CVOO	F		NT*						

*Multinet Midi (Hydrobios); sampling depths (vertical): 800-500m, 500-300m,300-200m, 200-100m, 100-surface; 0.25 m2 net opening, 200 µm mesh size

	BIOMASS						RATES		
	Phytoplankton	**Microplankton**	**Zooplankton**	**Viruses**	**Bacteria & Cyanobacteria**	**NOTES**	**Primary Production**	**Bacterial Production**	**NOTES**
BATS (inc. Hydrostation "S")	F✠	FC	NT/DW♠		EF		14C	H3L	
Irminger Sea									
Iceland Sea									
Oceanic Flux Program									
SOUTH ATLANTIC									
Ubatuba	F								
Epea	EF/M (size-fractions: pico,nano,micro-phytoplankton; including cyanobacteria)		NT**		EF (heterotrophic bacteria)	For the ultra-phytoplankton Flow Cytometer is occasionally used	13C		Primary Production est. occasionally (when large vessel available) P&I incubation box (3 hs). Hama et al. 1983
SOUTHERN OCEAN									
Palmer LTER	F(T)✠		NT		FC		14C	H3L	
Southern Ocean Time-Series (SOTS)	M		A				O2/gas sensor		
King Sejong Station (KOPRI)	x								
INDIAN OCEAN									
Coastal Bay of Bengal (Vizag)			x				x		
Western Australia	x		x						

**Small-Bongo (67um-220um), obliquos tow (towing time: 2 min; towing rate: 20 m min-1). Specific biomass derived from abundance and mean individual biovolume following Viñas et al. 2010). Biovolumes are converted to wet weight applying a factor for specific gravity.

PART 6. Time-series measurements (inorganic carbon parameters, trap fluxes, organic matter)

	INORGANIC CARBON PARAMETERS					TRAP FLUXES				ORGANIC MATTER		
	TCO_2 (DIC)	**fCO_2/p CO_2**	**Total Alkalinity (TA)**	**pH**	**NOTES**	**C and N Flux (organic and inorganic)**	**P Flux**	**Si Flux**	**NOTES**	**Dissolved organic C, N, P**	**Particulate organic C, N, P**	**NOTES**
SOUTH PACIFIC												
Munida	C		P									
IMARPE (Callao)	C	S	P	P		MT			TECHNICAPPP S-3	HTC	EA	Perkin Elmer 2400 Series II CHN Analyzer
COPAS						MCl				HTC	x	
Eastern Australia	x	mooring (cont.)	x			MCl						
NORTH PACIFIC												
Japan (JMA)	C		S	S						HTC		
Japan (JAMSTEC)	C		S	P		MCl/DT		MCl/DT		HTC		
Ensenada	x		x	x						HTC	EA	
CalCOFI and CCE-LTER	C	x	P							HTC	EA	
MBARI	x		x								EA	
SPOT						x	x	x				
HOT	C		P	P		DT	DT	DT		HTC; UV oxidatation	PC, PN (EA♣), PP (HTC)	
Line P	C		P	S								
Station Papa	C		P	S								

	INORGANIC CARBON PARAMETERS					TRAP FLUXES				ORGANIC MATTER		
	TCO_2 (DIC)	**fCO_2/*p* CO_2**	**Total Alkalinity (TA)**	**pH**	**NOTES**	**C and N Flux (organic and inorganic)**	**P Flux**	**Si Flux**	**NOTES**	**Dissolved organic C, N, P**	**Particulate organic C, N, P**	**NOTES**
NEPTUNE Canada	x		x	x		x	x	x			POC, PON	
Santa Barbara Channel - Plumes and Blooms	x		x			x	x	x		HTC	POC, PON	
CARIBBEAN SEA												
CARIACO			S	S		MCl	MCl	MCl		HTC	EA	
Cartagena				P								
NORTH ATLANTIC												
Labrador Sea (BIO)	C		P	S						DOC	POC	
Offshore Halifax Line	C		P	S						DOC	POC	
Davis Strait	C		P	S								
Barrow Strait	C		P	S								
Hudson Bay and Strait	C		P									
PAP												
OWS M (Ocean Weather Station M)	C	mooring 2011- (Battelle pCO2 system and Sunburst pCO2)	P	mooring 2011- (Sunburst SAMI pH sensor)								
ESTOC	C		P	S							POC, PON 1994-1999 only (EA)	
A Coruña RADIALES (NW Spain)										HTC, TOC	EA	

	INORGANIC CARBON PARAMETERS					TRAP FLUXES				ORGANIC MATTER		
	TCO_2 (DIC)	**fCO_2/*p* CO_2**	**Total Alkalinity (TA)**	**pH**	**NOTES**	**C and N Flux (organic and inorganic)**	**P Flux**	**Si Flux**	**NOTES**	**Dissolved organic C, N, P**	**Particulate organic C, N, P**	**NOTES**
Cape Verde Ocean Observatory - CVOO	C		P		pCO2 is being measured on the mooring (see in-line meas.)	MCl				HTC	EA	No determination of P
BATS (inc. Hydrostation "S")	C		P			DT	DT			HTC, MAGIC	EA fuming filters	
Irminger Sea	C	Equilibration and GC or IR										
Iceland Sea	C	Equilibration and GC or IR										
Oceanic Flux Program						MCl	MCl	MCl			MassSpec, Lachat	also d13C,d15N
SOUTH ATLANTIC												
Ubatuba												
Epea										CDOM		
SOUTHERN OCEAN												
Palmer LTER	C		P			MCl	MCl	MCl		HTC	EA	
Southern Ocean Time-Series (SOTS)	x	mooring (cont.)	x			MCl	MCl	MCl		HTC	EA	
King Sejong Station (KOPRI)												
INDIAN OCEAN												
Coastal Bay of Bengal (Vizag)												
Western Australia	x	mooring (cont.)	x									

METHODS USED

Biomass/pigments

M = microscopy
FC = flow cytometry
F(T) = Fluorescence (Turner)
F = Fluorescence
DW = dry weight
A= Acoustic determination
B = Backscatter
NT = Net Tows
EF = Epifluorescence

Dissolved Organic Methods

HTC = High temperature combustion
MAGIC = MAGIC DOP method

Particulate Organic Methods

EA = Elemental Analyzer
HTC = High temperature combustion

CTD/discrete

W = Winkler titration
GP = Guildline Portasal
GA = Guildline Autosal
M = Minisal

DIC

C = Coulometer
P = Potentiometric
S = Spectophotometric

Nutrients

AA = Autoanalyzer
F = Fluorescence
M = manual spectrophotometry

Traps

MCl = Mclane Traps
DT = Drifting trap

In Line

IR = *p* CO_2 Infrared analysis

Rates

^{14}C = Radiocarbon
^{13}C = Carbon 13
O_2 = Oxygen uptake
H3L = Leucine Incorporation

NOTES

♣Filters are NOT acid-fumed prior to running for POC/PN
♠Dry weight is size-fractionated

Chl *a* Fluorescence

✠Acetone Extraction
⌘Methanol Extraction
❖Ethanol Extraction

Autoanalyzers

*continuous segmented flow (e.g., Technicon, Seal, Skalar, Quattro, etc.)
**flow injection analysis (e.g., Lachat)
▼rapid flow analyzer (e.g., Alpkem)
✧micro-segmented flow (e.g., Astoria)