CHAPTER 6

Biogeochemical In Situ Observations – Motivation, Status, and New Frontiers

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We begin this chapter on in situ biogeochemical observations by presenting the three major areas of societal benefit related to ocean observations: climate, operational ocean services, and ocean health. Biogeochemistry constitutes a varying proportion of each of these areas, while climate and ocean health benefit more from sustained flow of accurate information than operational ocean services. Once the societal drivers are presented, we focus on identifying the relevant phenomena that need quantifying. These phenomena are closely related to the scientific dimension, which helps to establish specific observing targets and observing system design. Scales, seasonality, and geographic limitations are briefly discussed. Consideration is also given to the fact that often a given biogeochemical phenomenon is primarily driven by physical processes (e.g., ventilation, air-sea fluxes) or biological and ecosystem mechanisms (e.g., organic matter cycling, eutrophication) and, therefore, parameters across all three disciplines ought to be measured. Next, we provide an overview of the current capabilities of the global ocean observing system (GOOS) for biogeochemistry. The capacity is considered as an ability (or lack thereof – a gap in capacity) to address the requirements stated in the earlier part of the chapter. A holistic approach to thinking about platforms and sensors is presented. In the following section, the data quality requirements and efforts, as well as data management practices are briefly explained. There has been a strong, long-standing effort among the carbon and biogeochemical observationalists to make biogeochemistry data not only freely available, but also quality-controlled and inter-comparable. These grassroots efforts eventually led to the successful creation of two information products: SOCAT and GLODAP, which are predominantly carbon-focused and represent almost exclusively ship-based, benchtop instrument-based observations. We also discuss an urgent need to expand biogeochemical data availability, quality control, and inter-comparability beyond carbon parameters and onto a wider suite of available platforms and observing techniques (sensors). Finally, to the extent possible, a perspective on existing and planned prototype technology is provided.

Global Ocean Observing System and the Framework for Ocean Observing

The ocean covers 70% of the Earth's surface and is the natural system that ultimately provides most of the air we breathe and the fresh water we drink. The ocean is the primary controller of the global climate that makes this planet habitable for humankind. The ocean is also the pathway for 90% of global trade, it provides 17% of the animal protein consumed by the world's human population, it is a huge draw globally for tourism, and it hosts 99% of the habitable space for our planet's animal and plant life, much of which we believe has not yet even been discovered. Sustainable use and development of the ocean, or the "blue economy", has tremendous

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potential to create jobs and economic value. The ocean is also changing. Shrinking ice caps, sea level rise, ocean acidification, degradation of coastal and open-ocean habitats, plastics and other pollutants, over-exploitation of fish populations, the death of coral reefs and other declines in biodiversity, extreme storms, and coastal flooding — these all pose increasing risks. Understanding, forecasting, and adapting to these growing risks urgently requires that more ocean information be collected, processed, and made available in better ways to support multiple users — governments for policy-making, businesses for safe and efficient operations on the seas and coastlines, scientists for greater understanding of ocean processes, and coastal citizens who are increasingly dependent on forecasts and warnings to protect them from local disasters (GOOS, 2018).

The Global Ocean Observing System (GOOS) and the Global Climate Observing System (GCOS) coordinate sustained observations around the global ocean for three critical themes: climate, ocean health, and real-time services. These themes correspond to the GOOS/GCOS mandate to contribute to the:

- United Nations (UN) Framework Convention on Climate Change (UNFCCC),
- UN Convention on Biological Diversity (CBD),
- Intergovernmental Oceanographic Commission of UNESCO (IOC-UNESCO), and
- World Meteorological Organization (WMO).

This mandate includes observations used for operational ocean services. Historically, these services were based mainly on information related to physical oceanography; however, over the past decade or so our needs for near real-time operational knowledge related to marine biogeochemistry has increased significantly, as did our overall capacity to deliver the required information. The ocean observing community has realized that many observational disciplines are needed to quantify the simultaneous impacts of multiple stressors on ocean ecosystems. This required a re-thinking of many observing strategies, and some compromises (within and across disciplines) have to be made in order to achieve a fit-for-purpose global ocean observing system

There are three broad areas where multidisciplinary sustained ocean observations can bring societal benefit:

- Climate. The ocean is a key component of the climate system and influences its evolution and change through the energy, water, and element cycles. Better monitoring and knowledge will inform both mitigation and adaptation to climate change as well as improved climate services.
- Operational ocean services. Coastal populations and infrastructure are growing and are increasingly exposed to ocean-related hazards. Also, the major marine industries and other ocean users continue to grow. Ocean forecasts and early warning systems can help manage risk and improve business efficiency.
- Ocean health. Ocean ecosystems are coming under increasing pressure from anthropogenic influences, through climate change (warming), acidifying and changing oxygen distributions, and direct human impact. Better monitoring and knowledge will help in sustaining livelihoods and ecosystem services from the ocean.

The impact of such multidisciplinary, sustained ocean observing system derives from a value chain (Figure 6.1) that links research and technology innovation; sustained observing systems; data management systems, analyses, syntheses, and information products; ocean forecast systems and scientific analysis; and operational services and scientific assessments to societal benefit.

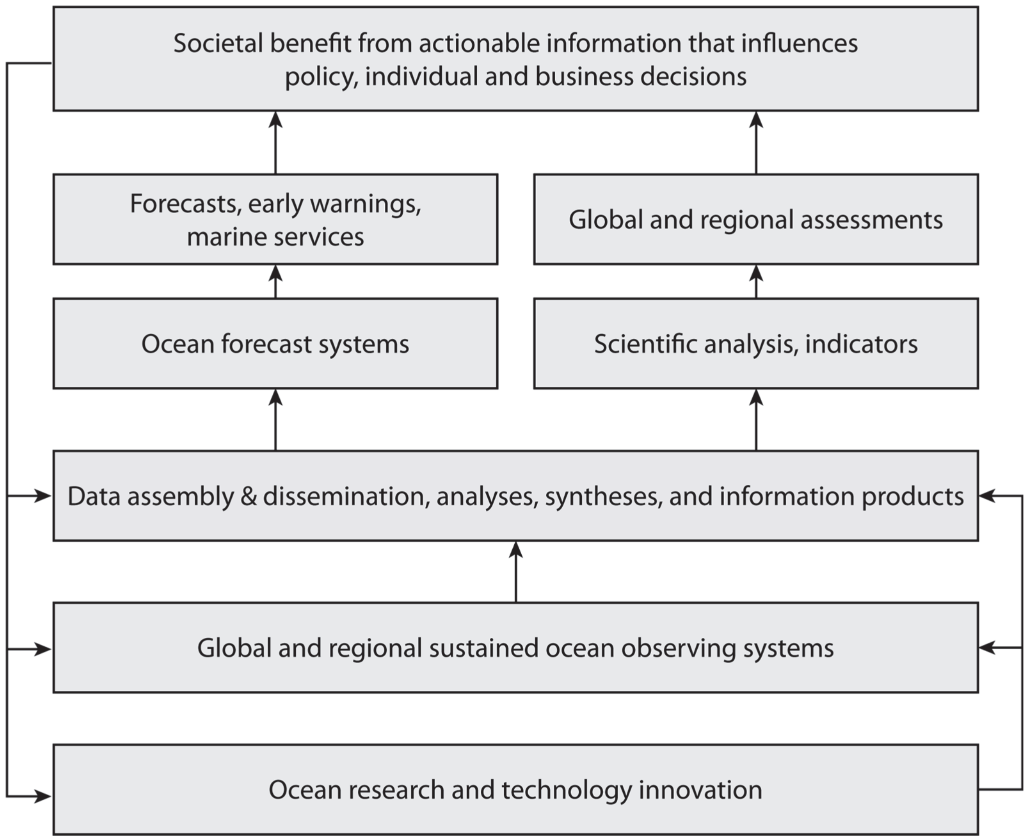

Figure 6.1. An illustration of the value chain linking sustained ocean observations with societal benefit. *Adapted from the G7 Ocean Expert Group think piece, May 2016.*

Improving the feasibility of sustained ocean observations benefits from a close alliance between ocean research and technology innovation, which has always been the source of the observing platforms and sensors that comprise sustained observing systems. Data from the observing system must then flow into systematic data assembly and dissemination centers where they can also be transformed into analyses, syntheses, and information products for use in scientific research or for direct input into indicator frameworks such as 2030 Agenda for Sustainable Development or ocean forecast systems. Here the value chain diverges somewhat into two paths based on our readiness to accurately model the phenomena in question: one through ocean and climate forecasting systems into forecasts, early warnings, and marine services that allow individuals and businesses to make decisions; and the second through scientific analysis or indicator frameworks to global and regional assessments and policy briefs that can inform government or business decisions and policy. This reinforces the dual purpose of a sustained infrastructure for operational benefits as well as for scientific research. The primary concern for operational services will be to estimate the state of the ocean and for scientific analysis and assessments to provide sustained observational infrastructure to understand phenomena and build knowledge.

In 2009, the global observing community agreed to develop and implement the global observing system that could deliver to the above value chain, incorporating information gathered across disciplinary-focused communities: physical oceanographers, marine biogeochemists, and biological oceanographers. Such homogenization of historically fragmented, discipline-based observing efforts required developing a fit-for-purpose strategy, where the main purpose would be addressing short- to long-term societal needs while preserving the well-being of the ocean ecosystem. A key recommendation from the OceanObs'09 Conference held in Venice in September 2009 (www.oceanobs09.net) was the international integration and coordination of interdisciplinary ocean observations. The conference was sponsored by many international and national ocean agencies and attended by representatives of ocean observation programs worldwide. Based on agreement among the many groups present and their strong desire to work collectively, the sponsors commissioned a task team to develop an integrated framework for sustained ocean observing.

The *Framework for Ocean Observing* (FOO, 2012) identifies lessons learned from the successes of previously existing ocean observing efforts and provides an internationally-accepted common language and guidance for expanded collaboration in sustained ocean observations (Figure 6.2). It is focused on:

- delivering a system based on common **requirement**s, coordinated ocean **observing elements**, and common **data and information streams**;
- Essential Ocean Variables (EOVs), a common focus for requirements defined based on *feasibility* and *impact* on societal and scientific drivers; and
- evaluation of "readiness levels" for each of these system components.

Societal needs and scientific requirements for biogeochemical observations

Surface fluxes are commonly thought of as the transfer of something (e.g., momentum, heat, moisture, a gas, or particulates) from the ocean to the atmosphere or vice versa. For such a transfer to be maintained, the fluxes must also apply on both sides of the air-sea interface, otherwise there will be a buildup or a loss at the ocean surface. For example, the latent heat flux is related to evaporation at the ocean surface, but is also the vertical transport of this energy in the atmospheric boundary layer. Stress is the vertical transport of momentum at the air-sea interface, but there must also be an identical transport of momentum in the atmospheric and oceanic boundary layers unless that momentum is released or transported away by waves in the process of crossing the air-sea interface. Consequently, we realize that air-sea fluxes modify the air-sea interface and could plausibly be measured from satellite. Again, understanding the geophysical processes that modify the surface and hence modify the electromagnetic characteristics of the surface can be useful in developing more accurate retrievals and retrievals of new variables.

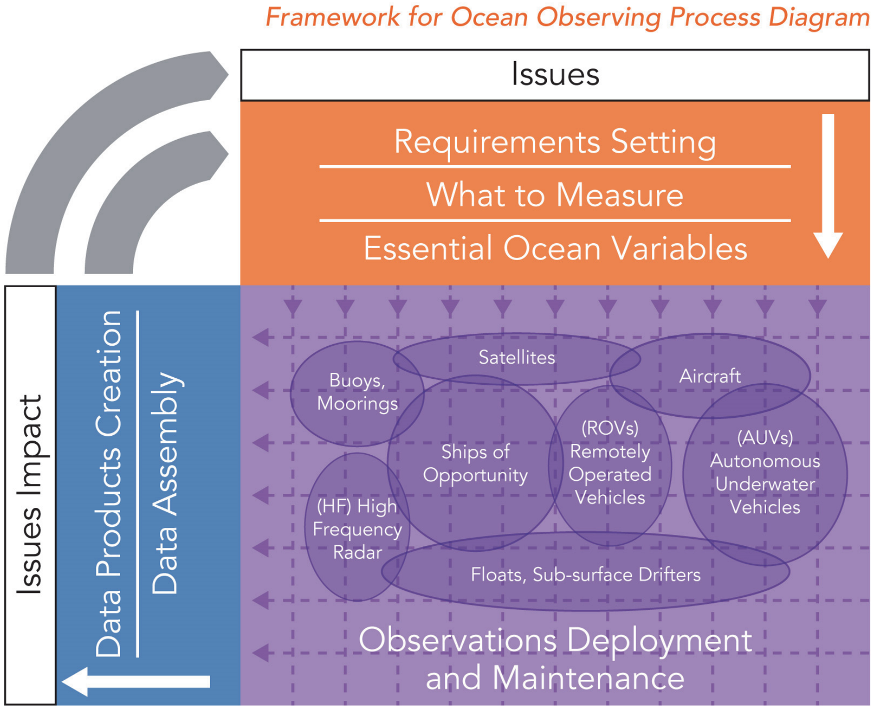

Figure 6.2. Processes in the *Framework for Ocean Observing,* with feedback loops in the definition of requirements and the outputs of the observing system, and a check for fitness-of-purpose of these outputs against societal drivers.

Experts representing a wide array of programs, institutions, national agencies, and inter-governmental and non-governmental organizations were consulted in order to develop a set of presently most pressing requirements related to marine biogeochemistry. Identifying a common approach to requirements across the stakeholders of multidisciplinary global sustained ocean observing systems facilitated developing a common understanding of the societal and scientific needs that facilitates the joint investment needed to build and maintain such an integrated multidisciplinary system. It also encourages integration of the existing elements of the observing system, ensuring that we can develop an infrastructure for both operational services and research. Several workshops, individual consultations with experts representing specific and narrow scientific fields, as well as open-access consultations during large-scale conferences led to agreement upon the following three overarching requirements, each of which is divided into two main questions:

The role of ocean biogeochemistry in climate

The oceans play a critical role in the cycling of many greenhouse gases. It is responsible for taking up and storing about 50% of the anthropogenic emissions of carbon dioxide since the pre-industrial era, thereby buffering (or mitigating) the rate of climate change. Other biologically active elements, such as nitrogen and oxygen, also play an important role in regulating the climate and its effects on how habitable our planet is, most notably through ocean ventilation and the so-called biological pump — the process of uptake of carbon by phytoplankton and its export to the ocean interior and sediments. Marine biogeochemical processes contribute to the complexity of ocean-atmosphere interactions and feedback mechanisms. Constraining the seasonal, regional, and global patterns of fluxes of carbon and other biologically active elements in and out of the ocean is critical to understanding the natural cycle of carbon in the ocean, and thus enhancing the capacity to predict how it might change in the future and what its effects on climate will be.

Key Questions:

How is the ocean carbon content changing?
As the biggest mobile reservoir of carbon in the earth system, any change in the ocean's ability to uptake and store anthropogenic carbon will have a direct impact on rates of atmospheric carbon dioxide (CO_2) concentrations, and hence on climate. Therefore, an observing framework that allows quantification and detection of change of both anthropogenic and total ocean carbon storage and uptake is critical (e.g., for setting emission targets, carbon accounting, model predictions, etc.). Additionally, understanding ocean oxygen fluxes and inventories are important indicators of ocean ventilation and respiration that are needed for more accurate carbon budgets.

How does the ocean influence cycles of non-CO_2 greenhouse gases?
The ocean is a key unknown in the cycling of many other non-CO_2 greenhouse gases such as ozone, depleting, e.g., halocarbons (methyl bromide, bromoform), methane, nitrous oxide (N_2O), and dimethyl sulfate. Ocean measurements are essential for closing the budgets of these gases, which are potentially strong amplifiers of climate change. Furthermore, an ocean observing system that allows for early detection would serve as a warning system alerting us to the risk of passing key tipping points in the climate system.

Human impacts on ocean biogeochemistry
Human activities, such as fossil fuel burning and industrial fertilizer production, have perturbed the global elemental cycles of carbon and nitrogen and significantly impact ocean chemistry. For example, shifts in the carbon chemistry of seawater, as well as changes in nitrogen and oxygen in both coastal and open ocean waters, have been widely recorded. These induce a variety of shifts in marine resources, the full impact of which we still don't understand. The rates at which these changes occur often exceed the recent geological record and highlight the need for a more comprehensive, multivariable approach to ocean biogeochemical analyses in order to better track and predict changes and impacts on marine ecosystems.

Key questions:

How large are the ocean's "dead zones" and how fast are they changing?
The oxygen content of the ocean is decreasing in many areas and, in particular, oxygen minimum zones (OMZ) are growing, likely due to combined effects of changes in circulation and rates of biological oxygen consumption. Oxygen is a strong habitat constraint for most marine animals, and OMZs are areas of highly reduced animal diversity. Low oxygen concentration leads to significant changes in biogeochemistry such as reduction of available nitrate, which can impact ocean productivity.

What are rates and impacts of ocean acidification?
Ocean acidity (i.e., the activity of hydrogen protons, H^+) has increased by 30% since the pre-industrial period. This acidification will likely have significant effects on all levels of the trophic chain (e.g., reproduction, ecosystem structure, physiology), directly impacting future food security. Changes and impacts are expected to be heterogeneous and more severe in the coastal ocean.

Ocean ecosystem health
Changes in ocean chemistry will directly impact the health of marine ecosystems and, as a result, affect humans that rely on marine resources for ecosystem services (e.g., food security, aquaculture).

Key Questions:

Is the biomass of the ocean changing?
Quantifying the magnitude of changes in ocean biomass and productivity, and separating natural variability and secular trends is crucial for understanding and mitigating future impacts on fisheries. Changes in nutrient supply and distribution of macro- and micronutrients are key drivers of primary productivity, which will be impacted by changes in the nitrogen cycle (e.g., nitrogen [N_2] fixation, denitrification). Understanding biogeochemistry changes is key to predicting potential impacts on food webs.

How does eutrophication and pollution impact ocean productivity and water quality?
Land-based sources of nutrients (macro and micro) and carbon (organic and inorganic) into the coastal ocean increasingly lead to eutrophication and hypoxia directly impacting productivity and leading to deleterious effects such as harmful algal blooms. Furthermore, human pollution caused by the use of persistent organic pollutants (POPs), plastics, and dioxins can adversely impact ecosystem health.

Phenomena and essential ocean variables

Minimum set of biogeochemical phenomena to quantify
In order to provide relevant quantifiable information that will allow us to address the above questions, we must develop or adapt an observing system so it is capable of monitoring a comprehensive list of relevant phenomena that control the ocean variability specifically in the context of these drivers. Defining biogeochemical phenomena is challenging, mainly due to the fact that many are either primarily driven by physical (e.g., ventilation, air-sea fluxes) or biological and ecosystem mechanisms (organic matter cycling, eutrophication). In addition to identifying the key phenomena of interest, which should actively drive the design of the global observing system, the spatial and temporal scales on which these phenomena operate need to be well understood. Each phenomenon operates on a variety of spatial and temporal scales that must be considered when choosing the most efficient measuring platform and sensor/instrument. Although the current observing system setup is not centered around phenomena, but rather around observing approaches

and/or individual EOVs, such a paradigm shift is much needed to move from a fragmented towards an integrated multiplatform and multidisciplinary observing system.

Here, we will define a phenomenon as follows (adopted from GOOS): *A **phenomenon** is an observed process, event, or property, with characteristic spatial and timescale(s), measured or derived from one or a combination of EOVs, and needed to answer at least one of the scientific questions asked in order to address relevant societal need.*

The following list of phenomena, with short descriptions given in terms of their biogeochemical relevance, has been adopted by GOOS. Whether in the context of operational oceanography, meaning short-term monitoring, or climate variability understanding, which requires decades of observations, these phenomena have to be quantified in parallel with "auxiliary" physical and biological measurements to enable the delivery of information required to address today's societal needs and scientific questions:

- Ventilation (water mass age)
- Air-sea fluxes
- Cross-shelf interactions
- Anthropogenic carbon sequestration
- Ocean acidity
- Inorganic nutrient cycling
- Organic matter cycling
- Hypoxia
- Eutrophication
- Contamination/pollution

Ventilation (water mass age)

Ocean ventilation describes the rate and pathways by which surface waters are carried into the interior of the ocean (e.g., Church et al., 1991), and it is the key physical process determining water mass age. Documenting long-term changes in water mass age and ventilation rates is a key requirement for understanding the role of biogeochemical cycling in climate. Ventilation occurs via a number of downward physical transport mechanisms, such as deep water formation, subduction processes (mode water formation), seasonal mixed layer dynamics, and diffusive fluxes.

Ventilation rates strongly affect biogeochemical cycling of elements, especially carbon, oxygen, and nutrients in the ocean (Sarmiento et al., 2004; Le Quere et al., 2007; Gille, 2008). Understanding the response of ventilation processes is critical now that we have begun to understand feedbacks between climate change and the rate of uptake of anthropogenic CO_2 (C_{ant}) by the ocean (Fung et al., 2005). Monitoring changes in ventilation strength through biogeochemical measurements helps answer the question of how is the ocean carbon content changing. Observing variability in ventilation strength on adequate spatial and temporal scales will greatly improve the constraints on modelling the role of ocean biogeochemistry in climate.

Spatial scales over which ventilation occurs range from local- to basin-scale, i.e., from 100 to 10,000 km. Timescales of ocean ventilation span from sub-annual to millennial, corresponding to water mass ages ranging from zero to 1,000 years. Detecting short-term changes in water mass age and associated changes in biogeochemical properties is important in the context of seasonal to interannual variability in biological production and carbon content in the ocean. However, the observing system should remain focused on documenting changes in ocean ventilation and resultant water mass ages on decadal and longer timescales. This variability is necessary to quantify long-term trends in C_{ant} ocean uptake or oxygen and nutrient storage in the ocean interior.

Air-sea fluxes

The surface turbulent fluxes of momentum, heat, and moisture at the interface between the atmosphere and the oceans represent an exchange of energy between the two. The air-sea fluxes are also an important phenomenon responsible for cycling numerous biogeochemical elements. Biogeochemical observations in the Atlantic focus on several types of air-sea fluxes: (i) air-sea fluxes of CO_2, (ii) air-sea fluxes of O_2, (iii) N_2O flux to the atmosphere, and (iv) dust deposition; observations of which help answer one or more of the GOOS scientific questions.

Air-sea fluxes of CO_2: Although currently not as important as ocean circulation and mixing, air-sea CO_2 gas exchange is one of the mechanisms controlling C_{ant} uptake by the ocean (Talley et al., 2016). For any particular location, the flux of CO_2 between the air and the sea is the product of two principal factors: 1) the difference in partial pressure of CO_2 between the air and the bulk water (ΔpCO_2), which can be considered as the thermodynamic driving force, and 2) the gas exchange rate or “transfer velocity” (k_w), which is the kinetic parameter. The transfer velocity incorporates both the diffusivity of the gas in water (which varies with temperature and between different gases), as well as the effect of physical processes within the water boundary layer.

The rate of CO_2 exchange is determined by the transfer across the water boundary layer; thus, the flux is obtained by multiplying the difference between the air and water pCO_2 (partial pressure of CO_2 in air, which is in equilibrium with the water) by the solubility "K_0" in mol l^{-1} atm.

Air-sea fluxes of oxygen (O_2): Two separate mechanisms contribute to trends in dissolved oxygen storage in the ocean. First, the air-sea flux component corresponds directly to the amount of oxygen (O_2) that the ocean is losing or gaining from the atmosphere, i.e., it is that part of the marine O_2 that leaves an imprint on atmospheric oxygen (Gruber et al., 2001; Keeling and Garcia, 2002). It is important to separate this component from the second mechanism that includes all processes at the surface and interior not associated with the exchange of O_2 across the air-sea interface, i.e. as a result of biological consumption and production of O_2 in the surface ocean and through physical transport and mixing (Stendardo and Gruber, 2012, and references therein). To quantify the contributions of these mechanisms driving the changes in oxygen, one needs to calculate trends in the saturation concentration of O_2, trends in the apparent oxygen utilization and trends in the quasi-conservative tracer O^*_2 derived from dissolved oxygen and phosphorus concentrations (Keeling and Garcia, 2002). Dissolved oxygen tends to respond very sensitively to climate variability and change because any perturbation in sea surface temperature not only changes the solubility of dissolved oxygen, but also alters upper ocean stratification in a way that tends to amplify the solubility effect (e.g., Najjar and Keeling, 2000; Keeling et al., 2010). This high sensitivity to climate forcing makes oxygen one of the best candidates for detecting, and thus better understanding the link between global warming and the resulting biogeochemical and physical changes in the ocean (e.g., Joos et al., 2003; Keeling et al., 2010).

N_2O flux to the atmosphere: Because of the ongoing decline of chlorofluorocarbons and the continuous increase of N_2O in the atmosphere (e.g., Machida et al., 1995; IPCC AR4; IPCC AR5), the contributions of N_2O to both the greenhouse effect and ozone depletion will be even more pronounced in the 21st century. The oceans — including coastal areas such as continental shelves, estuaries, and upwelling areas — are a major source of N_2O and contribute about 30% to the atmospheric N_2O budget. Oceanic N_2O is mainly produced as a by-product during archaeal nitrification (i.e., ammonium oxidation to nitrate), whereas bacterial nitrification seems to be of minor importance as a source of oceanic N_2O. N_2O also occurs as an intermediate during microbial denitrification (nitrate reduction via N_2O to dinitrogen, N_2). Nitrification is the dominating N_2O production process, whereas denitrification contributes only 7-35% to the overall N_2O water column budget in the ocean. The amount of N_2O produced during both nitrification and denitrification strongly depends on the prevailing dissolved O_2 concentrations and is significantly enhanced under low (i.e., suboxic) O_2 conditions.

Atmospheric dust deposition: Dust is produced primarily in desert regions and transported long distances through the atmosphere to the oceans. Once deposited, dust dissolution can be an important source of a range of nutrients, particularly $N_2$and iron, to microbes living in open ocean surface waters (Jickels and Moore, 2015). Direct measurements of $N_2$from dust deposition are difficult. The majority of flux estimates used come from particle tracking models, with assumptions about dust deposition solubility and bioavailability. Ship-based oceanic measurements of dissolved nutrients are needed in parallel with atmospheric measurements of dust deposition rates to further validate these models.

Cross-shelf interactions

This phenomenon describes the biogeochemical exchanges with shelf and marginal seas. In many coastal circulation regimes, the proximity of energetic boundary currents in deep water at the shelf edge is a key dynamic in mediating shelf/open ocean exchange. On coasts for which estimates exist, fluxes of nutrients and carbon across this boundary are leading order terms in the $N_2$and carbon budgets of shelf ecosystems. The exchange at the ocean boundary and shelf edge dynamics immediately impact ecosystem function and productivity on weekly-to-seasonal timescales; they can also drive multi-decadal changes in ecosystem structure via effects on habitat ranges and biodiversity.

Direct observations of biogeochemical and physical exchanges across the shelf-open ocean boundary have not been sustained to the extent required to fully complement observations within the ocean interior. In large part, this is due to the particular challenges of maintaining observing networks within energetic regimes, and capturing the significantly shorter time and space scales of variability there.

Quantifying nutrient fluxes across the shelf-open ocean boundary, often occurring in pulse form in response to passing fronts and eddies, is essential to inform, calibrate, and validate biogeochemical models, which can enhance the capacity for harmful algal bloom forecasting. Measurements of carbon and oxygen fluxes are another important application.

Anthropogenic carbon sequestration

The term "carbon sequestration" here describes only the natural oceanic processes by which CO_2 is removed from the atmosphere and stored in the ocean interior or buried in marine sediments. Given the accelerating pace of emissions related to human activities, it is important to explicitly detect changes in the uptake and storage of the anthropogenic component of CO_2 in the atmosphere, in addition to quantifying the ocean's role as a sink in the global carbon budget. By continuing to take up a substantial fraction of the C_{ant} emissions from fossil fuel combustion and net land-use change, the ocean is a major mediator of global climate change. Therefore, observing the phenomenon of anthropogenic carbon sequestration helps answer the question 'How is the ocean carbon content changing?'

Mechanisms of carbon sequestration are either physicochemical (through the solubility pump) or biological (through the biological pump), and are no different regardless of whether the sources of carbon are natural or anthropogenic (Raven and Falkowski, 1999). Several methods have been developed and tested to accomplish the separation between changes in dissolved inorganic carbon due to C_{ant} uptake and those due to natural variations in circulation and organic matter remineralization (Friis et al., 2005; Locarnini et al. 2013; Zweng et al. 2013). The physicochemical mechanism is closely related to two other phenomena discussed in this chapter, i.e., ventilation and air-sea fluxes. On the other hand, the biological mechanism relates to organic matter cycling. As a result, setting biogeochemical observing targets with respect to C_{ant} sequestration phenomenon should not be done in isolation from considering requirements for observations of these other phenomena.

Ocean acidity

Acidity is hydrogen ion (H+) concentration in a liquid, and pH is the logarithmic scale on which this concentration is measured. Ocean acidification is a progressive increase in the acidity (decrease in pH) of the ocean over an extended period, typically decades or longer, which is caused primarily by uptake of CO_2 from the atmosphere. It can also be caused or enhanced by other chemical additions or subtractions from the ocean. Acidification can be more severe in areas where human activities and impacts, such as acid rain and nutrient runoff, further increase acidity.

The pH of the open ocean surface layer is unlikely to ever become acidic (i.e., drop below pH 7.0) because seawater is buffered by dissolved salts. However, ocean acidification is changing seawater carbonate chemistry. The concentrations of dissolved CO_2, hydrogen ions, and bicarbonate ions are increasing, and the concentration of carbonate ions is decreasing. Changes in pH and carbonate chemistry force marine organisms to spend more energy regulating chemistry in their cells. For some organisms, this may leave less energy for other biological processes such as growing, reproducing, or responding to other stresses.

Many shell-forming marine organisms are very sensitive to changes in pH and carbonate chemistry. Corals, bivalves (such as oysters, clams, and mussels), pteropods (free-swimming snails), and certain phytoplankton species fall into this group. But other marine organisms are also stressed by the higher CO_2 and lower pH and carbonate ion levels associated with ocean acidification. The biological impacts of ocean acidification will vary because different groups of marine organisms have a wide range of sensitivities to changing seawater chemistry.

Aragonite saturation state is another indicator of change in ocean acidity. Aragonite is a mineral form of calcium carbonate, a basic building block of corals and many forms of zooplankton. The aragonite saturation state decreases with increasing acidity of ocean water. Below a certain threshold, calcifying organisms using aragonite cannot produce shells or skeletons effectively. Thus, changes in aragonite saturation state will become a broad-scale ocean ecosystem stressor that will affect a large set of organisms.

Aragonite saturation state in surface and subsurface waters is calculated from dissolved inorganic carbon and total alkalinity data. According to Jiang et al. (2015), through the year 2012 surface aragonite saturation state in the open ocean was always supersaturated ($\Omega > 1$), ranging between 1.1 and 4.2. It was above 2.0 (2.0–4.2) between 40°N and 40°S, but decreased toward higher latitude to below 1.5 in polar areas.

Inorganic nutrient cycling

Nitrogen in various forms occurs naturally in the environment, including inorganic species such as ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), and nitrogen gas (N_2), and organic forms such as amino acids, proteins, DNA, and RNA; the latter forms occur both as particulate and dissolved fractions. The phosphorus and silicon cycles are less complex but are equally important in controlling ocean biomass and carbon content changes.

The following processes reflect either sources or sinks of inorganic nitrogen in the ocean, and they require support from biogeochemical observations and modelling: (i) denitrification, nitrification and anaerobic ammonium oxidation (anammox), (ii) N_2 fixation, and (iii) non-point and point source nutrient fluxes.

Denitrification, nitrification, and anammox processes determine the availability of macronutrients for phytoplankton uptake. Denitrification reduces nitrate, first to nitrite and then to ammonia, burning oxygen. we often observe predominance of denitrification in OMZs and in coastal eutrophicated waters, thus further augmenting the loss of oxygen and leading to temporary or persistent hypoxia (i.e., oxygen reduced in concentration to a point where it becomes detrimental to aquatic organisms). Anammox is a significant component of the biogeochemical nitrogen cycle, whereby ammonia and nitrite are converted directly into nitrogen gas. Globally, this process may be responsible for 30-50% of the N_2 gas produced in the oceans (Devol et al., 2003). Therefore, it is a major sink for fixed nitrogen and it limits oceanic primary productivity. In the Atlantic Ocean, for example, anammox appears to be closely coupled to denitrification, with regional differences observed between the shelf and continental slope areas (e.g., Trimmer and Nichols, 2009).

Nutrient cycling on scales from hours (ammonia production) to seasons (nitrate replenishment in surface waters) affects patterns of phytoplankton community composition and primary productivity on scales from days to months. In combination with changes in the physical transport of new and regenerated nutrients, interannual or decadal changes in nutrient availability also affect the long-term variability in organic matter cycling.

N_2 fixation is a biologically mediate process in which atmospheric N_2 gas is converted into ammonia by prokaryotes called diazotrophs. N_2 fixation provides a means of fixing organic matter under reduced nitrogen availability conditions. Nevertheless, diazotrophs have strong requirements for phosphorus and iron. N_2 fixation is not directly measured in the ocean, but can be derived from measurements of available phosphate. The importance of this process increases as we move towards the equator and decreases towards the higher latitudes in the Atlantic, with some regional enhancements associated with boundary current regions.

Organic matter cycling

Organic matter cycling refers to a group of processes that either biologically transform or physically transport organic matter between the surface and interior ocean or across the water-sediment interface. Biological transformations of organic matter include gains due to fixation of atmospheric CO_2 and inorganic nutrients into particulate organic matter, as well as losses due to grazing and respiration that transform particulate into dissolved organic matter and organic carbon and nutrients back into their inorganic forms.

Organic matter fixation is particularly important with respect to the biological component of anthropogenic CO_2 uptake that results from net community production, defined as the gross primary production by autotrophs minus the total respiration by phytoplankton, zooplankton, and the resident microbial community. Globally, the magnitude of the net community production signal is estimated to be in the range of 5-15 Pg-C per year. In the Atlantic, the North Atlantic spring bloom has gained a lot of attention due to the uptake and potential sequestration of CO_2 via rapid growth of large phytoplankton cells (i.e., diatoms) and subsequent vertical export of assimilated carbon to depth following nutrient limitation. The highly seasonal nature of the diatom bloom, specifically the rapid growth and equally rapid export of cells during bloom termination, as well as the patchy nature of the bloom makes this phenomenon particularly difficult to study. Higher-resolution sampling in time and space is required to capture the smaller, episodic events describing the coupled physical and biogeochemical dynamics of the spring bloom.

The oligotrophic waters of subtropical ocean gyres occupy >40% of the Earth's surface; thus, even relatively low carbon exports in these immense ocean provinces may significantly contribute to the global carbon budget. While surface ocean biology is very similar between two Atlantic central gyres, there is an established spatio-temporal variability in their upper ocean biogeochemistry. Presence of such a signature in the deep ocean has long been unknown due to a lack of direct measurements.

Changes in organic matter fixation and remineralization, and resultant amount of particulate carbon export into the ocean interior, occur over a broad range of timescales, from weekly to interannual and longer. However, as shown by Henson et al. (2016), detecting long-term climate-driven trend in changing biological production and export might require temporal records substantially longer than what is available beyond a few existing time series stations. Except for a very few regions where natural variability signal is relatively weak, in most areas of the global ocean, records between 25 and 50 years might be necessary to detect climate-driven trends in these processes. This is also significantly longer than chlorophyll a (Chl-a) observations available from remote sensing.

Considering a limited number of open ocean fixed-point observatories and their limited spatial footprint of 42-43 10^6 km^2 (defined as the area over which a station is representative of a broader region; Henson et al., 2016), this represents a significant gap in the observing system capacity to answer the question of how does the ocean carbon content change, at least on long-term scales.

Dissolved organic carbon (DOC) is one of the largest bioreactive pools of carbon in the ocean (Hansell et al., 2009; 2012). The inventory of oceanic DOC is estimated to be ~662 ± 32 Pg C, 200 times the mass of the organic carbon in suspended particles but approximately 1/50th of the total dissolved inorganic carbon inventory (Hansell et al., 2009). The majority of the newly produced DOC is rapidly remineralized by heterotrophic bacterioplankton within the ocean's surface layer (Carlson and Hansell, 2015). However, ~20% of global net community production (~1.9 Pg C year−1) escapes rapid microbial degradation for periods long enough to be exported from the euphotic zone via convective mixing or isopycnal exchange into the ocean's interior (e.g., Hansell et al., 2009). DOC export occurs with deep- and mode-water formation as mid-latitude, warm, DOC-enriched surface waters are transported with surface currents to subpolar and high latitudes. Here, convective overturn transports the DOC deep into the interior, where it is slowly removed through southward flow.

Hypoxia

Hypoxia is the result of a process of decomposing organic matter (mostly phytoplankton) biomass that uses up dissolved oxygen in the water in equilibrium with a certain rate of oxygen flux by ocean transport processes (phenomena: circulation, mesoscale transport). It can occur naturally, or be stimulated by anthropogenic nutrient pollution through non-point and point sources (see also eutrophication below).

Changes in oxygen content in the ocean have a direct impact on both the climate and ecosystem health. The concentration of dissolved oxygen is a major determinant of the distribution and abundance of marine species globally. Open ocean deoxygenation has already been recorded in nearly all ocean basins during the second half of the 20th century. Increased temperatures are responsible for approximately 15% of the observed change, and the remaining 85% is due to reduced O_2 supplies from increased ocean stratification and deep-sea microbial respiration (IOC-UNESCO and UNEP, 2016).

Although deoxygenation is the predominant direction of change in the ocean, this trend is not uniform across ocean basins. In the North Atlantic, for example, although the upper, mode, and intermediate waters are indeed losing oxygen because of changes in solubility, the deeper waters actually gained oxygen over the last 50-year period owing to changes in circulation and ventilation (Stendardo and Gruber, 2012). Oxygen decline is found most consistently in the OMZs

Although seasonal or persistent OMZs occur on local (up to 100 km) scales frequently in the coastal ocean, in the open ocean Atlantic the main areas of interest with respect to the observing system are upwelling regions. These regions present a very complex case where several phenomena are inter-linked with each other, through a myriad of physical, biogeochemical, and biological processes. The schematic on Figure 6.3 illustrates the complex interaction between coastal hypoxia and eutrophication and open ocean oxygen conditions only found in some upwelling regions (Doney, 2010).

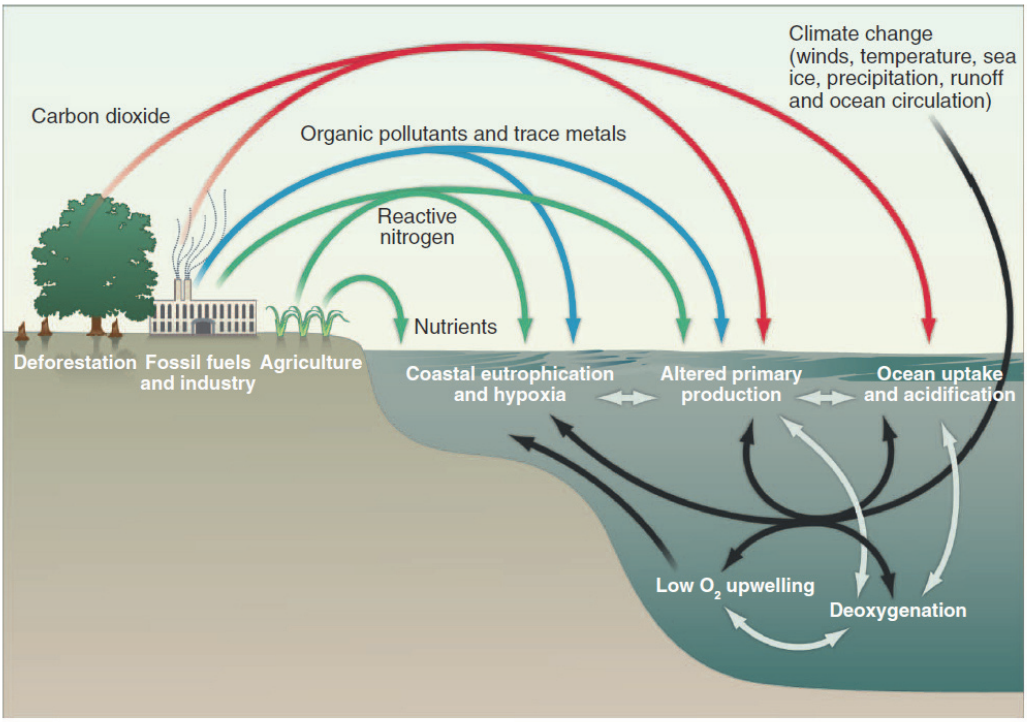

Figure 6.3. Schematic of human impacts on ocean biogeochemistry either directly via fluxes of material into the ocean (colored arrows) or indirectly via climate change and altered ocean circulation (black arrows). Source: Doney, 2010.

<u>Eutrophication</u>

Monitoring and predicting the eutrophication status of waters is an important part of determining whether an ecosystem is in a healthy state or not. The eutrophication is driven by a surplus of the nutrients nitrogen and phosphorus in the sea, caused mainly by agriculture activities (fertilizer use and wastes from livestock) and urban wastewater. Nutrient over-enrichment, also referred to as nutrient pollution, causes elevated levels of algal and some plant growth, increased turbidity, oxygen depletion, changes in species composition, and increase in toxins (e.g. through incidence of harmful algal blooms). As these properties and events are directly measurable or are easily derived from such measurements, eutrophication is observed based on its impacts on biogeochemistry and biology, rather than being observed based on the state of its pressures and drivers such as excess concentration of nutrients in river run-off or atmospheric deposition. This has implications for selecting core indicators of eutrophication and designing an observing system adequate for monitoring changes in eutrophication status. Observing changes in eutrophication is tightly coupled with three other phenomena: inorganic nutrient cycling, hypoxia, and organic matter cycling.

Contamination/pollution

Marine water pollution is a significant concern for ocean ecosystem health. The following contaminants are generally identified: plastics, organic contaminants, heavy metals, hydrocarbons, and underwater noise.

Plastic debris or litter in the ocean is now ubiquitous. Durability is a common feature of most plastics and it is this property, combined with an unwillingness or inability to manage end-of-life plastic effectively, that has resulted in marine plastics and microplastics becoming a global problem. We distinguish between floating macro and microplastics, and there is also a pool of mid-water microplastics. At the moment, our ability to detect floating plastics is limited to presence/absence data, but future sustained efforts to measure their concentrations (e.g., through underway automated data capture instruments) would help constrain the current, very large level of uncertainty on their distribution.

Persistent, bioaccumulating, and toxic organic compounds (PBTs) are also ubiquitous in the marine environment, primarily because of human activity. These include a category called persistent organic pollutants (POPs), which are either banned or restricted under the Stockholm Convention. Some are hydrophilic and others are hydrophobic. Many of these compounds have chronic impacts on marine organisms, especially at higher trophic levels amongst top predators. There are human populations, particularly at higher latitudes, directly affected due to consumption of traditional foodstuffs.

There has been extensive research and development to produce sensors that can make in situ sampling by employing a concentration stage, using passive samplers with lower detection limits based on a variety of gel and films (e.g., Burgess et al., 2015).

Floating plastics, PBTs, and POPs remain in the natural system on similar temporal scales, from weeks to decades. Due to their wide-spread transport in the ocean, they affect the marine system in spatial scales from meters to thousands of kilometres.

Atmospheric deposition is the main source of dissolved heavy metals in the ocean (cadmium, copper, lead, zinc, cobalt, zinc, mercury, methyl mercury). The partitioning of atmospheric inputs between dissolved and particulate phases within the surface layer strongly determines the behaviour of trace metals and their involvement in biogeochemical cycles (Cossa et al., 2009). Basically, the assimilation of metals by biota may be constrained by their solubilisation, resulting from physicochemical and biological processes (dissolution through zooplankton intestines, for example). Riverine fluxes are the main source of heavy metal particulates. Distribution of heavy metals changes in annual scales, and spatially, from 100-3000 km when affected by atmospheric deposition and from 1-1000 km when driven by river inputs.

Minimum set of biogeochemical variables to measure

EOVs are the *Framework for Ocean Observing* concept of the fundamental physical, biogeochemical, and biological measurements needed for the scientific understanding of ocean phenomena and the provision of applications in support of societal needs. What makes these observables essential is that they are the minimum subset required; they are not replaceable by other variables. Their essential nature is defined by both a:

- high *feasibility* of sustained observation, based on the platforms and sensors that can observe this variable at the space and timescales and accuracy needed to capture the required phenomena, and
- high *impact* of the observation in creating the application or contributing to the needed scientific knowledge, and therefore providing societal benefit.

EOVs are basic variables observable by one or more practical instrumentation systems. Measuring the whole suite of defined EOVs is necessary to provide the data to quantify all the phenomena in support of scientific research and address societal issues related to the ocean and climate. EOV specification sheets linking EOVs to societal benefits describe: their importance in scientific phenomena, present observation strategies (e.g., spatial and temporal resolution, accuracy, technological readiness level), required complementary variables, derived variables, and the observation programmes and networks measuring the data. Specification sheets for marine biogeochemistry EOVs briefly described below can be found at http://www.ioccp.org/index.php/foo. There are nine biogeochemical EOVs (listed below).

Dissolved Oxygen

Measuring and understanding the large (mostly) decreasing trends in the concentrations of dissolved oxygen in the ocean over the last few decades has important implications for our understanding of anthropogenic climate change. Sub-surface oxygen concentrations in the ocean reflect a balance between supply through circulation and ventilation and consumption by respiratory processes. An observing network of dissolved oxygen, among other things, results in the following products: (i) improved constraint on the ocean-land-partitioning of anthropogenic CO_2, (ii) determination of the seasonal to interannual net remineralization rates as a proxy for the amount of organic matter exported from the surface ocean, (iii) better interpretation of variations in water mass ventilation strength, (iv) and increased availability of crucial data (initial conditions, evaluation) for ocean biogeochemistry models.

Nutrients

The availability of inorganic macronutrients (NO_3, phosphate [PO_4], silicon [Si], ammonium (NH_4), nitrogen dioxide (NO_2)) in the upper ocean frequently limits and regulates the amount of organic carbon fixed by phytoplankton, thereby constituting a key control mechanism of carbon and biogeochemical cycling. There is a number of biogeographic regions in the open ocean characterized by different macronutrient regimes, either permanently or seasonally limiting the growth of phytoplankton. Measuring changes in macronutrient concentrations is essential to constraining net biological production and export fluxes, detecting shifts in biogeographic regimes, but also monitoring eutrophication and pollution phenomena.

Inorganic Carbon

The observations required to constrain the carbon system at a point in space and time are any two of dissolved inorganic carbon, total alkalinity (T_{ALK}), partial pressure of carbon dioxide (pCO_2) and pH, and associated physical variables (temperature and salinity). High resolution and long-term observations of the carbonate system are essential for distinguishing the climate change-driven trends from the strong seasonal to decadal variability signal in net biological production and export flux, in particular in the high-latitude spring bloom systems. The carbon system is in a delicate balance such that high quality observations and predictions of the carbonate system will continue to be required to have a mechanistic understanding and ability to predict the changes in the anthropogenic carbon flux and storage in the interior ocean, and ocean acidification rates.

Transient Tracers

Transient tracers are a group of (chemical) compounds that can be used in the ocean to quantify ventilation strength, transit time distribution and transport time-scales. These compounds are all conservative in sea-water, or have well-defined decay-functions, and a well-established source function over time at the ocean surface. Measurement of transient tracers in the interior ocean thus provides information on the time-scales since the ocean was ventilated, i.e. in contact with the atmosphere. Knowledge of the transit time distribution of a water-mass allows for inference of the concentrations or fates of other transient compounds, such as anthropogenic carbon or N_2O. Commonly measured transient tracers are the chlorofluorocarbons (CFCs) 11 and 12, although in the past also CFC-113 and CCl_4 have been measured. More recently, measurement of transient tracers includes Sulphur hexafluoride (SF_6), radioactive isotopes 14C, tritium (decaying to stable 3He), and argon isotope 39Ar.

Particulate Matter

Particulate matter include the variables referred to as particulate organic matter (i.e. particulate organic carbon and particulate organic nitrogen; but also particulate inorganic carbon and biogenic silica (BSi); as well as the vertical transport (export) flux of all particulates. Observation of particulate organic matter within a global observing system would directly address the question of whether the ocean's biomass and productivity are changing. Changes in particulate organic matter could be important indicators of deteriorating water quality due to eutrophication in coastal regions, and of declines in primary production that could potentially translate up the food chain negatively impacting fisheries. Observation of particulate inorganic carbon would directly address the question of what impacts does ocean acidification have on calcareous organisms and, thus, community structure. Export production gradients occur over a multitude of spatial and temporal scales, therefore high spatial resolution measurements are needed (for example, in upwelling areas in the eastern boundary currents), while high temporal resolution measurements are needed, particularly in polar regions where spring blooms can be highly pulsed and the bulk of annual export rates occur often over only a few weeks' time.

Nitrous Oxide (N_2O)

The oceans, including its coastal areas such as continental shelves, estuaries, and upwelling areas, are a major source of N_2O and contribute about 30% of this important climate-relevant trace gas to the atmospheric budget. Because of the ongoing decline of chlorofluorocarbons and the continuous increase of N_2O in the atmosphere, the contributions of N_2O to both the greenhouse effect and ozone depletion will be even more pronounced in the 21st century. A ship-based observing network in the

Atlantic Ocean not only helps estimate global N_2O emissions but also helps capture information about ocean phenomena such as deoxygenation, eutrophication, and upwelling.

Stable Carbon Isotopes

Recent improvements in measuring the carbon-13 to carbon-12 isotope ratio (13C/12C) and concentration of CO_2 gas dissolved in seawater using field portable spectrometers open up the possibility of underway 13C/12C observations across large portions of the surface ocean. Such datasets would substantially improve δ13C-based estimates of organic matter export rate and of the air-sea $13CO_2$ flux. The latter term can be compared to depth-integrated $13CO_2$ inventory changes in the water column to provide a separation of anthropogenic CO_2 change due to air-sea CO_2 flux versus change due physical transport by ocean circulation. One example of a recent application of this approach in the North Atlantic indicates that 50% of the anthropogenic CO_2 increase in this ocean basin is a result of transport from the South Atlantic as part of the meridional overturning circulation.

Dissolved Organic Carbon (DOC)

DOC exceeds the inventory of organic particles in the oceans by 200-fold, making it one of the largest of the bioreactive pools of carbon in the ocean, second only to dissolved inorganic carbon. The size of the reservoir (comparable to that of atmospheric CO_2), as well as its role as a sink for autotrophically-fixed carbon, a substrate to heterotrophic microbes, and a sink/source of carbon involved in climate variations over long timescales, highlights its importance in the ocean carbon and nitrogen cycles. DOC exported from the epipelagic zone contributes around 20% to the biological pump via meridional overturning circulation.

Ocean Colour

Ocean colour radiance is the wavelength-dependent solar energy captured by an optical sensor looking at the sea surface. The spectral distribution of the water-leaving radiance contains information on the ocean albedo and optical constituents of the seawater, in particular the concentration of the phytoplankton pigment chlorophyll-a (a proxy for phytoplankton biomass). Deriving ocean colour products is not easy because the water-leaving radiance signal is relatively weak at the altitude of a satellite sensor (only 5-15% of incident solar radiation, with the remaining light having an atmospheric origin).

Ocean colour radiometry observations from space have revealed decadal-scale changes in the ocean biosphere. Passive ocean colour sensors observe only the first (top) optical depth of the ocean (40-60 m in the open ocean to less than 1 m in turbid coastal waters). However, when coupled with in situ observations and numerical models, these space-based observations provide a three-dimensional understanding of ocean processes, their complexity, and their interactions with other parts of the Earth system. Therein, enhanced in situ sampling of ocean colour and ecosystem variables is a requirement and a complement to satellite-based data.

Societal Drivers	Scientific Questions	Biogeochemical Phenomena to Capture	EOVs
The role of ocean biogeochemistry in climate	How is the ocean carbon content changing?	Ventilation (water mass age)	Transient tracers, oxygen, stable carbon isotopes
		Air-sea fluxes	Oxygen, inorganic carbon, N_2O , nutrients
		Anthropogenic carbon sequestration	Inorganic carbon, transient tracers
		Organic matter cycling	Oxygen, inorganic carbon, nutrients, suspended particulates, DOC, transient tracers
		Cross-shelf interactions	Oxygen, nutrients, inorganic carbon, suspended particulates, DOC
	How does the ocean influence cycles of non-CO_2 greenhouse gases?	Air-sea fluxes	N_2O, oxygen
Human impacts on ocean biogeochemistry	How large are the ocean's "dead zones" and how fast are they changing?	Hypoxia	Oxygen
	What are the rates and impacts of ocean acidification?	Ocean acidity	Inorganic carbon
Ocean ecosystem health	Is the biomass of the ocean changing?	Organic matter cycling	Oxygen, nutrients, inorganic carbon, Suspended particulates, DOC
		Inorganic nutrient cycling	Nutrients
	How does eutrophication and pollution impact ocean productivity and water quality?	Eutrophication	Oxygen, nutrients, suspended particulates, DOC
		Hypoxia	Oxygen
		Contamination/pollution	NA

Table 6.1. Links between societal drivers, scientific questions, and corresponding identified biogeochemical EOVs.

Table 6.1 summarizes the links between societal needs (drivers), scientific questions, and corresponding identified biogeochemical EOVs. This table indicates the central role of phenomena in the process of implementing the GOOS and provides a synthetic view of why and what needs to be observed in terms of marine biogeochemistry. The following two sections focus on the question: How?

Era of Biogeochemical Observations – New Frontier for Operational Oceanography

Current and expanding capacity for biogeochemical observations

All observing elements (platforms) organized into observing networks are characterized by time and space sampling, which are ultimately set by the technology. By combining the observing elements in the integrated GOOS, the sampling limitations of the individual observing elements can be minimized and a more comprehensive time and space sampling can be achieved; thus, addressing the observing objectives in a more complete way. The combination of the observing elements in a system is closely related to the capacities of an integrated GOOS. Despite the integration, unresolved time, space, and parameters remain – a fact that is closely related to the gaps of the system and which might be overcome by technological advancement and engineering. The maturity of the observing elements, particularly that of sensors, can be categorized in different levels of technical readiness. The Framework of Ocean Observations categorizes nine levels in three categories: requirement setting, observing capacity and data and information products delivery (Figure 6.4 below).

Biogeochemical EOV specification sheets indicate technical readiness levels for each category specifically for each observing element. Overall, a global ocean observing system for biogeochemistry based on the major networks described below has reached a satisfactory technical readiness level to address the current scientific questions globally. That might not be the case regionally and several processes remain unresolved due to technological shortcomings.

<u>Ship-based repeat hydrography</u>

Despite numerous technological advances over the last several decades, ship-based hydrography remains the only method for obtaining high-quality, high spatial and vertical resolution measurements of a suite of physical, chemical, and biological parameters over the full water column. Ship-based hydrography is essential for documenting ocean changes throughout the water column, especially for the deep ocean below 2 km.

The Global Ocean Ship-Based Hydrographic Investigations Program (GO-SHIP; http://www.go-ship.org/) helps develop a globally-coordinated network of sustained hydrographic sections (i.e., repeat hydrography) as part of the global ocean/climate observing system, providing information on physical oceanography, the carbon cycle, marine biogeochemistry, and ecosystems. GO-SHIP provides approximately decadal resolution of the changes in inventories of biogeochemical variables (such as carbon, oxygen, nutrients, and transient tracers), covering the Atlantic and other ocean basins from coast to coast and full depth (top to bottom), with measurements of the highest required accuracy to detect these changes.

The ship-based hydrography observing network is critical to addressing questions of how the ocean will respond to an increase in dissolved inorganic carbon, a decrease in pH, and changes in ventilation strength processes. Repeated decadal since the 1970s, these observations are a crucial resource for documenting baselines and patterns of long-term variability in many of the Atlantic

Ocean biogeochemical phenomena considered: ocean ventilation, anthropogenic carbon sequestration, organic matter cycling, hypoxia, and ocean acidity, both regionally and on basin-scale. GO-SHIP data also provide reference data to calibrate autonomous platform sensors that cannot be recovered, and cruises provide a stage for the deployment of many autonomous platforms as well.

Considering only the status of decadal full GO-SHIP lines, this observing network has lines distributed every approximately 20°, providing along-section sampling every 30 nautical miles. Such a sampling design is adequate for studying interannual to decadal variability in basin-scale signals for many of the key biogeochemical phenomena discussed above. Considering the availability of GO-SHIP data since the 1970s, these records are also long enough to detect climate-driven trends in key biogeochemical EOVs.

FRAMEWORK PROCESSES BY READINESS LEVELS

Readiness Levels	Requirements Processes	Coordination of Observational Elements	Data Management & Information Products
Mature			
Level 9 "Sustained"	Essential Ocean Variable: • Adequate sampling specifications • Quality specifications	System in Place: • Globally • Sustained indefinitely • Periodic review	Information Products Routinely Available: • Product generation standardized • User groups routinely consulted
Level 8 "Mission qualified"	Requirements "Mission Qualified:" • Longevity/stability • Fully scalable	System "Mission Qualified:" • Regional implementation • Fully scalable • Available specifications and documentation	Data Availability: • Globally available • Evaluation of utility
Level 7 "Fitness for purpose"	Validation of Requirements: • Consensus on observation impact • Satisfaction of multiple user needs • Ongoing international community support	Fitness-for-Purpose of Observation: • Full-range of operational environments • Meet quality specifications • Peer review certified	Validation of Data Policy • Management • Distribution
Pilot			
Level 6 "Operational"	Requirement Refined: • Operational environment • Platform and sensor constraints	Implementation Plans Developed: • Maintenance schedule • Servicing logistics	Demonstrate: • System-wide availability • System-wide use • Interoperability
Level 5 "Verification"	Sampling Strategy Verified: • Spatial • Temporal	Establish: • International commitments and governance • Define standardized components	Verify and Validate Management Practices: • Draft data policy • Archival plan
Level 4 "Trial"	Measurement Strategy Verified at Sea	Pilot project in an operational environment	Agree to Management Practices: • Quality control • Quality assurance • Calibration • Provenance
Concept			
Level 3 "Proof of concept"	Proof of Concept via Feasibility Study: • Measurement strategy • Technology	Proof of Concept Validated: • Technical review • Concept of operations • Scalability (ocean basin)	Verification of Data Model with Actual Observational Unit
Level 2 "Documentation"	Measurement Strategy Described • Sensors • Sensitivity • Dependencies	Proof of Concept: • Technical capability • Feasibility testing • Documentation • Preliminary design	Socialization of Data Model • Interoperability strategy • Expert review
Level 1 "Idea"	Environment Information Need and Characteristics Identified: • Physical • Chemical • Biological	System Formulation: • Sensors • Platforms • Candidate technologies • Innovative approaches	Specify Data Model • Entities, Standards • Delivery latency • Processing flow

Figure 6.4. A detailed description of varying readiness levels defined by the Framework for Ocean Observing. Source: FOO, 2012.

Ship-based underway observations

The Joint Technical Commission for Oceanography and Marine Meteorology Ship Of Opportunity Programme (SOOP) makes use of volunteer merchant ships that routinely transit strategic shipping routes. A number of biogeochemical EOV measurements depends on the SOOP network coverage. So-called 'underway' measurements of pCO_2 in surface sea water and in the air are made routinely by the SOOP network with high accuracies achieved. The SOOP pCO_2 data, potentially supplemented in the near future with underway measurements of pH, dissolved inorganic carbon, or total alkalinity, will be vital in describing basin-wide changes in the carbonate system, thereby improving seasonal and inter-annual climate predictions, and better constraining annually updated calculations of the global carbon budget.

Underway surface pCO_2 observations provide the capacity to constrain the air-sea CO_2 fluxes in key regions of the global ocean, on timescales from monthly to decadal. Combined with ocean interior observations collected on GO-SHIP lines, these measurements enable well-constrained estimates of carbon storage in the ocean.

The biggest limitation of using the underway ship-based observations from volunteer/commercial ships is the fact that we cannot directly alter the sampling scheme. Therefore, any spatial gaps (e.g., the South Pacific) or seasonal biases (e.g., boreal winter measurements in deep water formation regions in the North Atlantic) cannot be alleviated from the level of observing system design, but instead require installing a new pCO_2 line on an existing commercial vessel.

Fixed-point observatories

Single-point time series stations have increased understanding of the patterns of temporal variability but, by their nature, remain limited in the spatial domain. Henson et al. (2016) attempted to analyse the spatial footprint of moored fixed-point observatories with biogeochemical EOVs measured on them. They concluded that depending on the variable of interest, these footprints account for only 10-15% of the global ocean.

The fact that existing time series stations are representative of relatively large surface areas of the ocean confirms their role in estimating sub-basin scale patterns of variability. However, it is clear that much of the Atlantic, as well as the global ocean, remains under-sampled. There is a need to build and maintain a basin-wide and global network of multi-disciplinary, fixed-point surface and subsurface time series using mooring, ship and other fixed instruments, and to establish a coordinated network of ship-based multidisciplinary time series that is geographically representative.

Implementing this target will depend on the development of units attempting to coordinate fixed-point observatories. The Fixed-point Open Ocean Observatory (FixO3) network seeks to integrate European open-ocean, fixed-point observatories and to improve access to these key installations for the broader community. A similar mission, but on the global scale is adopted by OceanSITES, the goal of which is to collect, deliver, and promote the use of high-quality data from long-term, high-frequency observations at fixed locations in the open ocean. OceanSITES typically aims to collect multidisciplinary data worldwide from the full-depth water column as well as the overlying atmosphere.

Another key aspect of enhancing the fixed-point observatory capacity is the need to provide accurate information with which moorings can actually measure any of the biogeochemical EOV and, in the long-run, expand on the number of biogeochemical measurements performed routinely at time series stations.

In terms of the key geographic regions samples by fixed-point observatories, there is a gap in such measurements in places of deep water formation. Although resolving sub-decadal variability in basin-scale ventilation is not a primary goal for the observing system, weekly-to-seasonal variability in air-sea fluxes, inorganic nutrient cycling, and organic matter cycling are all crucial to understanding how the ocean carbon content and biomass are changing. While there transport mooring arrays exist in these key locations, there is a lack of coincident biogeochemical observations.

Profiling floats

Although Argo profiling floats can be considered a mature observing approach as far as technological readiness level is concerned, the newly-formed global biogeochemical Argo array as a coordinated observing network remains in pilot stage. There is currently a limited number of floats with biogeochemical sensors deployed.

Biogeochemical-Argo is set to enable direct observation of the seasonal- to decadal-scale variability in net community production, the supply of essential inorganic nutrients transported from deep waters to the sunlit surface layer, ocean acidification, hypoxia, and ocean uptake of CO_2. Bio-optical sensors would supplement ocean colour satellite observations by providing measurements of chlorophyll, light, and light scattering deep into the ocean interior throughout the year, in cloud- and ice-covered areas, or during the dark of polar winter.

The regional profiling float arrays equipped with biogeochemical sensors provide a sampling of ocean conditions around the world designed to produce an integrated dataset that can be used to address questions related to physical-biogeochemical coupling in eddies, phytoplankton phenology (cyclic and seasonal phenomena), nutrient supply, and climate effects on ocean carbon cycling in selected regions. Some of these arrays include:

- the Southern Ocean Carbon and Climate Observations and Modelling (SOCCOM) project,
- the Remotely Sensed Biogeochemical Cycles in the Ocean (remOcean) project in the North Atlantic subpolar gyre,
- the Novel Argo Ocean Observing System in the Mediterranean Sea (NAOS),
- the Integrated Physical-Biogeochemical Ocean Observation Experiment (INBOX) in the Kuroshio region of the North Pacific, and
- the Australia-India Joint Indian Ocean Bio-Argo Project (IO Bio-ARGO).

When setting targets for and optimizing the Biogeochemical-Argo array of floats, there is an inherent trade-off between meeting the requirements for observing relevant phenomena on adequate spatial and temporal scales, and the cost of maintaining a sustained observing network. Currently, the set target of deploying 1,000 biogeochemical floats is based on the results of a series of observing system simulation experiments performed by the SOCCOM team. That experiment revealed that the biggest gain, in terms of reducing the air-sea CO_2 flux reconstruction error, is between 500 and 1,000 randomly distributed floats. Hence, the target is currently 1000 floats (Johnson and Claustre, 2016)

The regional profiling float observation programs are also building the expertise needed to operate a global network that interacts with other components of the GOOS, including satellites (IOCCG, 2011), shipboard programs such as GO-SHIP, and various time series stations.

Currently, the size of the Biogeochemical-Argo array is insufficient to resolve many of the phenomena on basin-scale. Until a denser network is developed, they should be viewed as providing high spatial and temporal data on local to regional scales (1–1000 km), which are complementary to the basin-scale, decadal-scale ship-based repeat hydrography observations.

Gliders

Underwater gliders have enhanced capabilities, when compared with profiling floats. They provide some level of manoeuvrability and, hence, position control. The gliders perform sawtooth trajectories from the surface to depths of 1000-1500 m, along reprogrammable routes (using two-way communication via satellite), and they can be operational for several months. Their role in the integrated observing system is to fill the gaps left by other observing platforms. The mission of the EGO (Everyone’s Gliding Observatories; http://www.egonetwork.org/) underwater glider network is to develop a new observational capacity for process studies and operational monitoring of the ocean physics and biogeochemistry with gliders, and thereby go beyond the marine sciences frontiers. In particular, gliders could be deployed to sample most of the western and eastern boundary circulations and the regional seas, which are not well-covered by the present ocean observing system, as well as in the vicinity of fixed-point time series stations. Gliders can operate at higher resolution than the ca. 300 km/10-day float in the Argo profiling float network, and the even sparser ship-based observations. Therefore, glider-based observations have great potential to address regional and coastal issues, which are so important for societal applications.

Remote sensing observations

The space-based observing system is an important component of the GOOS. An array of geostationary and polar-orbiting satellites operated by the National Aeronautics and Space Administration (NASA) and the European Space Agency (ESA) sample the Atlantic and global surface ocean on unprecedented spatial and temporal scales, weaving together the requirements for observing surface signatures of key biogeochemical phenomena on short- and long timescales, providing basin-wide coverage with a simultaneous high spatial resolution on the order of kilometers.

Many products are derived from remote sensing observations that provide often unique information on a number of sub-variables listed under the particulate matter and dissolved organic carbon biogeochemical EOVs. Observations provided by the Ocean Colour Radiometry Virtual Constellation, and recently also by the LIDAR (light detection and ranging) method, enable near real-time monitoring of phenomena such as organic matter cycling and eutrophication. On the other hand, the focus of remote sensing observations is often on the physical and biological phenomena.

There are often very few algorithms available to estimate biogeochemical properties of interest, e.g., DOC or particulate inorganic carbon. Promoting new and alternative algorithms should be a goal that will lead to decreasing the high uncertainty of satellite-based measurements of biogeochemical variables.

Remote sensing observations are essential to studying surface processes related to organic matter cycling in key regions of the global ocean such as boundary currents and upwelling regions. Although much more challenging and associated with very large uncertainties, coastal satellite observations also provide information about changing carbon content on the continental shelf and in marginal seas regions.

The table below (Table 6.2) summarizes the links between the major observing elements and the biogeochemical EOVs that they measure (green indicates autonomous, blue indicates ship-based, and orange indicates remote sensing). Spatial and temporal scales captured by the observing elements measuring individual biogeochemical EOVs are described in the respective biogeochemical EOV specification sheets

Observing element	**EOVs (sub-variables measured)**
Profiling floats	Oxygen, nutrients (NO_3), inorganic carbon (pH), particulate matter
Gliders	Oxygen, nutrients (NO_3), inorganic carbon (pCO_2, pH), particulate matter
Moorings	Oxygen, nutrients (NO_3), inorganic carbon (pCO_2, pH), particulate matter
Drifting buoys	Nutrients (NO_3), inorganic carbon (pCO_2, pH)
Sediment traps	Particulate matter
Ship-based hydrography (including repeat hydrography)	Oxygen, nutrients (NO_3, PO_4, Si), inorganic carbon, transient tracers, particulate matter, N_2O, stable carbon isotopes, dissolved inorganic carbon
Ship-based time series^	Oxygen, nutrients (NO_3, PO_4, Si), inorganic carbon, N_2O, stable carbon isotopes, dissolved inorganic carbon
Ship-of-Opportunity	Oxygen, nutrients (NO_3, PO_4, Si), inorganic carbon (pCO_2, dissolved inorganic carbon*, pH*), particulate matter, N_2O*, stable carbon isotopes
Satellites	Particulate matter

Table 6.2. Links between major observing elements and biogeochemical EOVs measured by these elements.

Data quality and availability

There has been a strong, long-standing effort among the marine biogeochemistry observing and modelling community to make biogeochemistry EOV data not only freely available, but also quality-controlled and inter-comparable. These grassroots efforts eventually led to the successful creation of two information products: Surface Ocean CO_2 Atlas (SOCAT; Bakker et al., 2016) and GLODAP (Lauvset et al., 2016; Olsen et al., 2016). However, the data and synthesis products handled by SOCAT and GLODAP are predominantly carbon-focused and represent almost exclusively ship-based observations. There is an urgent need to expand biogeochemical data availability, quality control and inter-comparability beyond carbon parameters and onto a wider suite of available observing elements.

Vast number of metadata queried in, for example, European Union databases (e.g., SeaDataNet) is in fact under restricted access. Any access restriction, even as minimal as registration on the website through which data is to be acquired, prevents such data from being considered open-access and inevitably hinders data sharing. One example is the availability of in situ chlorophyll-*a* (Chl-*a*) and other pigment data from the British Atlantic Meridional Transect (AMT) cruises. These data, being of fundamental importance to calibration and validation of remote sensing-derived ocean product algorithms (for Chl-*a*, plankton size classes, plankton functional types, etc.), appear in SeaDataNet under restricted access. However, the same data is freely available through the US-based source, NOMAD: the NASA bio-Optical Marine Algorithm Dataset, available for download from: https://seabass.gsfc.nasa.gov/wiki/NOMAD.

N_2O is an example of an EOV observation for which a comprehensive, global database, MEMENTO (MarinE MethanE and NiTrous Oxide; https://memento.geomar.de/home) exists. While MEMENTO data is freely usable, access to the database is restricted (i.e., granted upon request via email). Although this could be considered a 'light' restriction, it is responsible for a gap in the observing system from the perspective of open access to information products that directly answer one of the key biogeochemical scientific questions: 'How does the ocean influence cycles of non-CO_2 greenhouse gases?'.

Future Prospects

The main focus for enhancement of the current biogeochemistry observing system is on sensor technology development. The sensor suite that is now available and tested throughout the array of autonomous and moored platforms (oxygen, pH, nitrate, chlorophyll fluorescence, and backscattering and downwelling irradiance sensors) is hardly sufficient to address the needs and questions driving the requirements for observations described above. These biogeochemical sensors are a relatively recent development and reflect the rapid expansion of technological capabilities that has resulted from the rapid development of electronics and optics over the past decade. It is likely that yet-to-be-developed sensors will enable significant extensions to the current capabilities. It is also possible that the existing sensors may be improved significantly. This has already happened for oxygen, for example. Early biogeochemical floats and gliders used oxygen sensors based on Clark-type oxygen electrodes (Edwards et al., 2010; Riser and Johnson, 2008). These have been replaced with optical sensors based on fluorescence lifetimes, which have improved stability and a capability for calibration in air (Körtzinger et al., 2005). New sensors that might be available in the future include pCO_2 sensors. The current state of optode-based pCO_2 sensors (Atamanchuk et al.,

2015) has not yet reached deployment-readiness. However, the pCO_2 sensor is expected to enable measurements of a prospective second carbon system parameter that may mature quickly and become an alternative to the pH sensor, allowing for direct observation of the CO_2 saturation state at the sea surface. This sensor, when installed on autonomous platforms, would also link directly with the pCO_2 measurements provided by the global ship-based networks, adding the much-needed vertical dimension. Other examples might include the development of particulate inorganic carbon sensors (Guay and Bishop, 2002) or fast repetition rate fluorometers. The highest accuracy pH measurements are generally made by spectrophotometry using well-characterized indicator dyes (Clayton and Byrne, 1993). Spectrophotometric pH profiles have been measured in situ (Liu et al., 2006) and such systems may become alternate approaches for pH determination if they are proven to have the appropriate performance needed for long-term deployments. Also, electrochemical sensors for N_2O, phosphate, oxygen, and silicate, as well as new optodes for pH, CO_2, O_2 and ammonia have been developed and are being tested. As new sensors are proven robust and effective, they may be considered for addition to the system based on performance, cost, and scientific merit.

In addition to new sensors, the performance of existing sensors may also be extended. One example might be application of the ultraviolet nitrate sensor to also observe dissolved nitrite in OMZ regions. The nitrite ion has a ultraviolet spectrum that is moderately distinct from that of nitrate (Johnson and Coletti, 2002) and quantification of the higher nitrite concentrations that result from denitrification in OMZ regions may be feasible. Such a capability would greatly add to interpretation of nitrate loss processes in OMZ regions.

Teams across the globe continue to push the sensors along the technology readiness levels, seeking to make their sensors commercially available as soon as possible. Issues such as power and resource management, internal and external communication, and expanding from single-parameter sensors to multi-parameter sensors are just a few of the myriad of challenges that need to be addressed.

Conclusion

Marine biogeochemistry observations are well-justified, well-designed and well-implemented, more so than ever before. Our understanding of the inter-connectedness of ocean processes requires a multidisciplinary and multi-parameter approach, whether we focus on operational oceanography or climate variability. There is still a large space for improvements in delivering integrated information products across disciplines, platforms, and parameters for the benefit of the informed ocean management. Potential benefits cannot be overstated and the efforts to operationalize all ocean observations, no matter how demanding they might initially seem, should not be neglected.

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