Pressures on the marine environment and the changing climate of ocean biogeochemistry

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The oceans are under pressure from human activities. Following 250 years of industrial activity, effects are being seen at the cellular through to regional and global scales. The change in atmospheric CO₂ from 280 ppm in pre-industrial times to 392 ppm in 2011 has contributed to the warming of the upper 700 m of the ocean by approximately 0.1°C between 1961 and 2003, to changes in sea water chemistry, which include a pH decrease of approximately 0.1, and to significant decreases in the sea water oxygen content. In parallel with these changes, the human population has been introducing an ever-increasing level of nutrients into coastal waters, which leads to eutrophication, and by 2008 had resulted in 245,000 km² of severely oxygen-depleted waters throughout the world. These changes are set to continue for the foreseeable future, with atmospheric CO₂ predicted to reach 430 ppm by 2030 and 750 ppm by 2100. The cycling of biogeochemical elements has proved sensitive to each of these effects, and it is proposed that synergy between stressors may compound this further. The challenge, within the next few decades, for the marine science community, is to elucidate the scope and extent that biological processes can adapt or acclimatize to a changing chemical and physical marine environment.

Keywords: climate; ocean; acidification; deoxygenation; hypoxia; eutrophication

1. Introduction

Biogeochemistry is the study of biological, chemical, physical and geological processes and their interactions within and upon their environment. The cycling of carbon, nitrogen and other elements is essential to the efficient functioning of the biosphere and, from a Gaian perspective [1], is the controlling mechanism that ensures homeostatic control of the Earth’s environment, making it suitable for habitation. In recent decades, it has become apparent that our environment, including the oceans and biogeochemical cycles, is under pressure from anthropogenic forcing [2]. On local and global scales, these pressures (which include among others eutrophication [3], warming [4], deoxygenation [5] and acidification [6]) have the potential to alter the biological, chemical and physical characteristics of the oceans [7], and their understanding will continue to challenge the scientific community for the foreseeable future.

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International efforts, which have included initiatives such as the Joint Global Ocean FluxStudy (JGOFS), Integrated Marine Biogeochemistry and Ecosystem Research (IMBER), World Ocean Circulation Experiment (WOCE) and Surface Ocean Lower Atmosphere Study (SOLAS), have sought to implement or foster large-scale investigations of the contemporary ocean. Each has had its own goals but they are intrinsically connected through their over-arching objectives. Foremost is the aim to progress our understanding of the present marine environment in order to predict the potential response of the ocean to the pressures that may affect its function in the coming century. To take this understanding further requires the determination of how the role of the ocean may feed into the whole Earth system and ultimately impact on the social and economic requirements of the human population.

The UK has been instrumental in the development and delivery of these programmes and will continue to be so, albeit during a period of increased financial pressure. Recent organizational activity has seen the initiation of the multi-agency-funded UK Ocean Acidification Programme (www.oceanacidification.org.uk) and a revision of the Natural Environment Research Council (NERC) strategy document in order to reorganize the focus on biogeochemical cycles and the interactions between the surface and deeper parts of the Earth system (www.nerc.ac.uk/research/themes/earthsystem). There is a significant challenge associated with the integration of ocean biogeochemistry into Earth system science, but there is an obligation on society to meet this challenge in order to comprehend the extent of this changing environment and how it may impact on the functioning of global-scale processes. A number of predicted changes are likely to alter the function of current regimes and challenge physical, chemical and biological processes: under a warming climate, the retreat and forecast disappearance of Arctic sea ice [8] is likely to promote the release of methane [9], carbon dioxide and other climatically active gases into the atmosphere, with parallel changes in ocean stratification, circulation [10] and the sequestration of carbon. The deoxygenation of the ocean [5] as a consequence of warming and enhanced stratification has implications for biogeochemical cycling and for the fauna that exist within the ocean interior. If the effects of ocean acidification [11,12] follow some predictions, then there will be shifts in biological community structure and activity throughout the oceans.

The rate of progress in technological and procedural development that has accompanied recent research has been exceptional. From an instrumental point of view, this has included laboratory and shipboard hardware, autonomous vehicles (including gliders and Autosub) and remote sensing. Progress in methodology has challenged existing paradigms [13], facilitated the tracking of water movement and air–sea exchange [14], discovered the most abundant photosynthetic cell on the planet [15] and provided tools to interrogate the genetic composition and activity of whole communities [16]. This degree of advancement will need to continue, not necessarily in instrumentation but certainly in application, in order to efficiently and economically improve our understanding of the intricacies of ocean biogeochemistry. Twenty years ago, the deployment of autonomous instrumentation, molecular biology, remote sensing and real-time oceanography from shipboard instrumentation were all in their infancy. Today, they are routine procedures that are relied upon to return an extraordinary amount of information. The UK and international biogeochemistry communities have
at their disposal fantastic research facilities and operational platforms, which include coastal and offshore mesocosms, as well as ships and long-time-series observatories. The Continuous Plankton Recorder (CPR) survey that is operated by the Sir Alistair Hardy Foundation for Ocean Science has been collecting data from the North Atlantic and the North Sea on the ecology and biogeography of plankton since 1931. More recently, HOT and BATS—the Hawaii Ocean Time-series (http://hahana.soest.hawaii.edu/hot/hot_jgofs.html) and Bermuda Atlantic Time-series Study (www.bios.edu/research/bats.html)—were initiated at sites in the Pacific and western Atlantic, respectively, while AMT—the Atlantic Meridional Transect (www.amt-uk.org)—offers an annual transect over approximately 100° of latitude through the Atlantic Ocean. We are charged as a community with the challenge to determine the sensitivity of the ocean to the stressors acting upon it and on the role that ocean biogeochemistry will play in mitigating the impact of change on the Earth system and human society.

2. The recent history of ocean biogeochemistry

To perform a review of 20 years of ocean biogeochemistry requires the production of a dedicated digest far beyond this paper, and indeed several bodies of work that provide excellent reviews are already published and made available [17,18]. This section provides a summary review of recent biogeochemical research to set the context of the current condition in order to address concerns for the ocean that are both current and relevant to subsequent decades.

(a) The JGOFS era

The determination of what we now consider to be the fundamentals of biogeochemistry are not necessarily based on new developments. A number of techniques, paradigms and datasets that underpin current oceanographic practices were developed over the last century:

— 1927 development of the Winkler titration for O₂ analysis [19];
— 1930s initiation of English Channel Time-Series of nutrients [20];
— 1952 ¹⁴C method for primary production [21];
— 1967 ¹⁵N method for new production [22]; and
— 1979 f-ratio as estimate of carbon export [23].

Ocean biogeochemistry really came to the fore though in the mid- to late 1980s. The impetus provided from the US Global Ocean Flux Study and the excitement that was generated by the production of the first basin-scale chlorophyll image in 1986 (figure 1) by Gene Feldman at NASA led to the initiation of the JGOFS (1987–2003) with the aim [24]:

-to assess more accurately, and understand better the processes controlling, regional to global and seasonal to interannual fluxes of carbon between the atmosphere, surface ocean and interior, and their sensitivity to climate changes.

The first internationally integrated study of ocean processes soon followed, with the North Atlantic Bloom Experiment (NABE) [25] in 1989, which involved

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Figure 1. The first global-scale chlorophyll image produced from the CZCS in 1986. This image heralded the use of satellite imagery in modern biogeochemistry and provided the impetus to Earth system science. This CZCS image was obtained from the NASA Ocean Colour website; I acknowledge assistance from the NERC Earth Observation Data Acquisition and Analysis Service.

ships from the USA, UK, Canada, Germany and the Netherlands, and with more than 12 nationalities represented on these vessels. Not only did this study unite the nations in their joint efforts, but it proved to be a significant multidisciplinary effort in consolidating previously disparate oceanographic disciplines into a concerted study of the biological, chemical and physical characteristics of the pelagic North Atlantic during the biologically active period of spring and summer. The success of this initial effort prompted further JGOFS coordinated campaigns to key oceanographic areas, which included the Southern Ocean, Arabian Sea and Equatorial Pacific.

The outputs from this work were almost revolutionary in their impact and contributed significantly to the shape of future research in this field and how we view the nature of biogeochemistry today. That mesoscale circulation was intimately connected to the dynamics of phytoplankton activity, that primary production was strongly linked to variability of CO₂, and that nitrogen regeneration was active throughout the bloom period, with regenerated production strongly linked to small cells, do not now seem surprising in any way.

(i) Ocean time series

Long-term time series have proved to be instrumental in resolving trends in natural variability and in the examination of external pressures on the marine ecosystem. The CPR survey has provided a significant insight into the sensitivity of North Atlantic plankton populations to climate and human-induced changes, which are discussed in detail with respect to the sustainable management of European seas by McQuatters-Gollop in this issue [26].

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At about the same time as JGOFS was coming into being, funding was provided by the US National Science Foundation (NSF) to establish the HOT and BATS time series at deep-water positions in the western North Atlantic and eastern North Pacific [27]. These two programmes in parallel with others around the world (DYFAMED, ESTOC, KERFIX, KNOT, OSP and SEATS in the Mediterranean, northeast Atlantic, Southern Ocean, southwest subarctic Pacific, northeast subarctic Pacific and South China Sea, respectively) have made repeat observations of biogeochemical and physical parameters on a regular basis since 1988. Through efforts at these stations, our understanding of ocean processes has been advanced to recognize the dynamic nature of the world’s oceans and the occurrence of regime or ecosystem shifts on variable time scales. Previously recognized paradigms have been challenged, including those concerning new production as defined by Dugdale & Goering [22] and elemental stoichiometry associated with the Redfield ratio [28]. We now recognize the importance of euphotic zone nitrification in the production of ‘regenerated’ nitrate, acknowledge the wide variability to be found in elemental ratios, and realize how both of these can have important implications on the efficiency of the biological carbon pump. As a direct result of work performed at HOT and BATS, nitrogen fixation was found to be integral to the productivity of the sub-tropical oceans, and the importance of diazotrophic unicellular cyanobacteria is now recognized alongside the more obvious filamentous *Trichodesmium* [29], which previously was held wholly responsible.

Following the early successes of these fixed-point time series, Aiken *et al.* [30] established the AMT in 1995. This is a regular (originally twice a year, currently annual) transect through the Atlantic Ocean between the UK and destinations in the South Atlantic (a distance of up to 13 500 km), which to date have been the Falkland Islands, South Africa and Chile. This programme has provided exceptional opportunities for biogeochemical oceanography through extremes of environment (temperate shelf, coastal upwelling, sub-tropical gyres, equatorial upwelling) and has delivered unique insights into biological carbon cycling and air–sea exchange of radiatively active gases and aerosols. Work performed during AMT cruises has refined definitions of ocean provinces [31], validated satellite algorithms [32], revealed hemispheric differences in hydrography and provided time-series assessment on basin scales [33].

(ii) The carbon cycle

During the early JGOFS research cruises, the refinement of analytical procedures to determine the carbon chemistry of sea water was significant in addressing the question of what controlled the variability of sea water $p$CO$_2$. One of the great achievements of this period, following close collaboration between JGOFS and WOCE, was the establishment of a global map of the temporal and spatial variability of air–sea CO$_2$ exchanges, and the identification of dominant CO$_2$ source and sink areas. Twenty years hence, and with the significance of CO$_2$ in sea water greater than ever, this technology is used to inform on process studies and to provide a network of observations using commercial ships. These data have proved essential in informing on the variability of the ocean sink for atmospheric CO$_2$ [34].
The Coastal Zone Color Scanner (CZCS) was the first instrument deployed in space to determine ocean colour. It was from this system that Feldman produced his basin-scale chlorophyll image, and although it was intended to provide coverage only for a 12-month period as a proof of concept, it remained in operation between 1978 and 1986. This proved invaluable in the development of procedures for early global estimates of primary productivity [35]. The launch of the successor to the CZCS, the SeaWiFS ocean colour scanner, was delayed by several years until 1997. This no doubt hindered the rate of progress during the major part of JGOFS, but the subsequent developments from the consolidation of ship-based observations with remotely sensed data were huge. This collaboration of efforts, which included modelled outputs, allowed the production of global composites of primary productivity and carbon export. Consequently, regions were identified in which oceanographic or biogeochemical processes were important in determining the degree of productivity and highlighting the importance of recycling and remineralization within the ocean interior.

The export of carbon from the upper to deep ocean through the biological carbon pump plays an important role in controlling the capacity of the upper ocean to hold atmospheric CO₂ and to remove C from active exchange with the atmosphere. The estimation of C export and the efficiency of the biological carbon pump are impacted by many variables and have been, and continue to be, approached with different methodologies. These include direct measurement using sediment traps and indirect estimates using the radionuclide thorium-234 and the $f$-ratio as a proxy for carbon export. The relationship between primary (new) production, export and deposition at the sea-bed was found to be regionally and temporally variable. This made prediction of carbon sequestration difficult, in part due to the large number of processes acting upon sedimenting material and to the strong dependence on the community composition from which the material originated [36]. The export of C is sensitive to a number of environmental stressors currently acting upon the oceans: phytoplankton communities are directly influenced by nutrient supply, and ballast material (calcite and opal) and aggregation processes may be impacted by ocean acidification [37].

A major assumption of biological oceanography has been that the metabolic balance between respiration and photosynthesis on appropriate scales of time and space must be equal. This was challenged by observations [38], which indicated significant regions and periods when respiration systematically exceeded production in large areas, leaving the ocean in a net heterotrophic condition. The resolution of this ocean enigma has yet to be found, and the debate continues over which of the two processes (photosynthesis or respiration) plays the dominant role in determining the balance between autotrophy and heterotrophy in the open ocean [39].

(iii) Nutrient limitation

Alongside the development of international collaborations and sampling observatories during the late 1980s and early 1990s, there were a number of hypotheses introduced that have challenged the ocean biogeochemistry community. In 1988, Martin & Fitzwater [40] published their seminal paper, which provided initial evidence supporting Martin’s hypothesis that Fe limited phytoplankton growth in high-nutrient low-chlorophyll (HNLC) areas of the
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oceans. An unprecedented number of laboratory, shipboard and mesoscale iron addition experiments evolved from this, each of which aimed to examine regional and seasonal variability in the degree of control by Fe over nutrient uptake, phytoplankton growth and carbon export to the deep ocean. The unequivocal findings from this work were that iron supply limits production in about one-third of the global ocean where surface macronutrient concentrations are perennially high and that iron exerts controls on the dynamics of plankton blooms, which in turn affects the biogeochemical cycles of carbon, nitrogen, silicon and sulfur, and ultimately influences the Earth’s climate system [41].

The concept of iron as a limiting nutrient in HNLC areas refuelled the long-running debate over which nutrient exerted overall control of oceanic primary production. Previously, this argument had largely been concerned with the relative influence of nitrogen and phosphorus [42], but with the recognition of the importance of nitrogen fixation, the role of iron, which is fundamental to the structure of several essential enzymes, including nitrogenase, as the ultimate limiting nutrient came to the fore. The debate over which single nutrient or combination of nutrients provides the dominant control continues [43,44], and is proving more relevant to our current understanding of the function of the oceans as we recognize the role of atmospheric dust and aerosol deposition as sources of iron, nitrogen [45,46] and other elements, and how this may alter under future climate change predictions.

A further development from mesoscale addition experiments was the use of sulfur hexafluoride (SF$_6$) as an inert, conservative tracer added in parallel to iron in order to track with great sensitivity the amended waters [14]. This technology has been used with great success not only in this mode but also as a means of estimating diffusive fluxes across pycnoclines [47] and fluxes across the sea–air boundary [48].

(iv) Ocean–atmosphere interactions

The deployment of SF$_6$, often in parallel with a second tracer (e.g. $^3$He), has been used to parametrize the gas transfer coefficient across the sea–air interface, which, in concert with gas concentration measurements, has enabled the identification of sink and source areas of numerous gases in the oceans and has contributed to our understanding of the role of the oceans in atmospheric chemistry and global climate. The oceans contribute 30 per cent of the natural N$_2$O source to the atmosphere, which is significant owing to its potency as an efficient greenhouse gas and stratospheric ozone destroyer. Other gases having oceanic sources that contribute to atmospheric chemistry include low-molecular-weight halocarbons and dimethyl sulfide (DMS). The CLAW hypothesis, as presented by Charlson et al. [49], suggested a negative feedback loop involving DMS, a compound produced and released under several mechanisms by marine phytoplankton. Following exchange with the atmosphere, DMS follows a step-wise pathway that, as was proposed, led to the formation of cloud condensation nuclei (CCN) and ultimately contributes to cloud formation and cloud albedo. The feedback loop responds to increases or decreases in solar insolation through altered rates of primary production. An increase in light increases primary production and therefore DMS production and so cloud albedo, which reflects incident sunlight, and thus the loop continues. While this would seem a potentially

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important mechanism to buffer the effect of a warming environment, evidence for the feedback loop is as yet equivocal [50]. A recent review of CLAW-related research also casts some doubt over the strength of the link between DMS emissions and CCN in the atmosphere [51] but raises an issue over the complexity of other marine sources of CCN that are relevant to this discussion on the role of the ocean in climate regulation. While the contribution of DMS to cooling of the planet is still not proved, Lovelock has suggested that enhanced stratification predicted as a result of warming may actually limit DMS production and provide a positive feedback loop where temperature rise is intensified [52].

(b) Other significant developments

During the last two decades, the pace of biogeochemical research has been maintained through parallel developments in remote sensing, modelling and molecular biology, so that these three fields are now integral to most observational research campaigns that are undertaken. As a result of these combined approaches, the contribution and role of previously unexpected new metabolic pathways that were revealed over the last 20 years using genomic and other techniques are now integral to routine biogeochemical investigations. These have included the discovery of anammox [53], the anaerobic oxidation of ammonium, which provides a pathway through to N$_2$ and contributes a poorly quantified part of denitrification in anoxic sediments and ocean basins. Until the late 1980s, the cyanobacterium *Prochlorococcus* was unknown. This organism, whose presence was detected through the advent of analytical flow cytometry [15], is now considered to be the most abundant photosynthetic cell in the oceans.

In the late 1980s and early 1990s, the ubiquitous abundance of marine viruses was recognized so that now they are considered to be the most diverse and numerous biogenic entities in the global marine biosphere, typically numbering ten billion per litre [54]. Through the process of infecting and lysing their hosts, viruses influence many biogeochemical and ecological processes, principally through their release of dissolved, available nutrients.

The advent of the polymerase chain reaction (PCR) led to the discovery of several groups of Archaea and, since then, they have been shown to be one of the most abundant unicellular groups in the ocean. Archaea are distributed in virtually all environments; Crenarchaeota have recently been recognized as the main drivers of the oxidation of ammonia to nitrite in the ocean, though the role of other Archaea in marine global biogeochemical cycles remains largely unknown [55].

Numerical modelling of the marine environment is an essential tool that gives us a means of synthesis and prediction and with which we can test our level of understanding. In 1990, Fasham et al. [56] introduced an ecosystem model designed to allow examination of seasonal cycles of plankton and nutrients in the global ocean in order to further the understanding of the role of the oceans in the regulation of atmospheric CO$_2$. This was to be the first stage in the development of coupled basin-scale models of ocean circulation with biogeochemistry. This compartmental (nutrients–phytoplankton–zooplankton–detritus; NPZD) model, which included plankton and nutrient dynamics, is still used as the basis of most ecosystem models. The use of nitrogen as a currency allowed, for the first time, for primary production to be partitioned into new and regenerated...
productivity, reflecting the relative uptake of nitrate or ammonium. Data from field programmes, from ocean time series and from satellite observations are used extensively in the development of new model formulations and in the validation of existing integrated model systems [57]. Doney et al. [57] reflect that the majority of modelling within JGOFS came at the end of the programme and was not used in the design of experimental approaches. A great legacy of JGOFS was a more sophisticated range of biogeochemical models that are now used as an integral component not only in the synthesis but also in the planning of observational oceanography. The continued development of biogeochemical models has resulted in the current generation of dynamic green ocean models (DGOMs). These are similar to NPZD models but have a much greater complexity and are based on plankton functional types. DGOMs aim to represent biogeochemical fluxes specifically associated with ecological processes [58] and have the potential to assess the effects of climate and environmental change on the ecosystem.

(c) IMBER and SOLAS

The mantle for ocean biogeochemistry coordination was taken from JGOFS by both the IMBER project (since 2001) and the SOLAS programme (since 2004). These two international programmes are complementary in their approach and have brought us to our present understanding of the contemporary ocean and the potential stressors that are likely to act upon it for the near future. IMBER was initiated by the IGBP/SCOR Ocean Futures Planning Committee in 2001, with the intention to identify the effects of global change on the ocean and the most important biological and chemical aspects of the ocean’s role in global change. IMBER has specific aims [59]:

- to investigate the sensitivity of marine biogeochemical cycles and ecosystems to global change, on time scales ranging from years to decades, and to provide a comprehensive understanding of, and accurate predictive capacity for ocean responses to accelerating global change and the consequent effects on the Earth System and human society.

SOLAS was developed to investigate the key climate linkages between sea and sky and involved over 26 countries and more than 1600 associated researchers, with the aim [60]:

- to achieve quantitative understanding of the key biogeochemical-physical interactions and feedbacks between the ocean and atmosphere, and of how this coupled system affects and is affected by climate and environmental change.

The ethos of both IMBER and SOLAS lies firmly within the spirit of Earth system science and has united traditional ocean biogeochemistry observations and models with atmospheric chemistry, climate models and remote sensing. This is an approach that will very much need to be followed into the future.

3. The current condition and future concerns

While our comprehension of the contemporary ocean is significantly greater now than ever before, pressures that act upon the biogeochemical cycles therein are
such that we are constantly playing catch-up in our need to fully understand the stressors, the synergy between stressors and their impacts on the ecosystem and its function. The next few decades will prove challenging as we strive to comprehend the extent of external stressors and the effect that they will have in disturbing natural systems, with a major challenge being to distinguish enforced change from natural variability. The impact of human activity over the last 200 years is now obvious and it is apparent that natural systems are being altered by anthropogenic inputs on regional and global scales (figure 2). Predictions into the near future indicate direct and indirect consequences of perturbations made to the environment by mankind’s activities that will act on oceanographic and biogeochemical functions [61]. Fossil fuel combustion and agriculture have contributed to climate change, and these areas each have significant influence over biogeochemical cycles in the ocean. Anomalous conditions relative to our current understanding of ocean and biogeochemical processes are associated with warming, acidification, deoxygenation and nutrient enrichment. Each condition brings its own individual challenge but is unlikely to exist without the contribution of one or more of the others.

(a) Climate change

It is without doubt that changes to our climate are happening and that the main driver for this is human activities [2]. Natural processes do contribute and include variations in solar radiation, deviations in the Earth’s orbit, plate tectonics and changes in greenhouse gas concentrations. Anthropogenic inputs of

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radiatively active gases (which include CH$_4$, N$_2$O, ozone and water vapour) to the atmosphere have increased since the industrial revolution, but it is CO$_2$ that has proved to be the dominant contributor to warming of the environment [62]. Atmospheric CO$_2$, following the burning of fossil fuels, cement manufacture and land-use change, has changed from 280 ppm prior to the industrial revolution to 392 ppm in 2011 and is forecast to be approximately 430 ppm by 2030. Mean global surface temperature rise during the twentieth century was 0.74$^\circ$C and, for the end of the twenty-first century, this is set to increase further in the range 1.5–6.1$^\circ$C, depending on CO$_2$ emissions. The upper 700 m of the ocean increased in temperature by approximately 0.1$^\circ$C between 1961 and 2003 [62]. For the period between 2003 and 2010, the ocean did not gain any significant amount of heat, though this is explained as a pause in the overall warming trend as a result of natural variability [63,64], and it would seem from recent observations that the warming trend is set to continue [63]. There remains considerable uncertainty about the details of spatial and temporal variability, but it is clear that climate change is fundamentally altering ocean ecosystems [65]. Although warming is the dominant direct effect, with impacts including sea-ice melting, changes to phytoplankton activity, and distribution and food-web shifts, there are indirect consequences that will also influence ocean biogeochemistry, including sea-level rise, pH change, increased stratification, shoaling of mixed-layer depths and changes to ocean circulation.

The effects of warming are being seen throughout the global oceans but it is in the polar regions where impacts are most significant, with unprecedented increases of winter surface temperature of 6$^\circ$C over 50 years for the West Antarctic Peninsula [66]. The Arctic is warming at about twice the rate of the global average, with recent studies showing that the area of the Arctic covered by ice each summer, and the ice thickness, have been shrinking [67] at unprecedented rates. These rapidly changing conditions impact the physical hydrography, which in turn influences changes in chemical and biological pathways. In the area of the Southern Ocean associated with the West Antarctic Peninsula, phytoplankton biomass has decreased by 12 per cent over the last 30 years, and there has been an apparent shift from large to small phytoplankton cells [63]. This has implications for the overall productivity of the region, as effects are seen across trophic levels, including impacts on even the region’s higher predators. In Arctic waters, the retreat of sea ice has been dramatic. Since records began in 1979, the extent of sea-ice coverage has decreased at an average rate of 12 per cent per decade, with 2011 having the second lowest cover (behind 2007), following higher than average summer air temperatures. The disappearance of the sea-ice cover has several implications, which include a positive feedback to warming as a result of a reduction in surface albedo, the release of methane (another potent greenhouse gas) following the destabilization of methane clathrates and the modification of sea-water stratification. Alterations to the salinity and temperature of surface waters are likely to alter local productivity in a manner similar to that described for the West Antarctic Peninsula, and may also impact on deep water formation and the Meridional Overturning Circulation—the driver for the Ocean Conveyor Belt [62].

There is some contention over the impact of a warming environment on the productivity of oceanic waters. Saba et al. [68] found, in a comparison of modelled and in situ data, that net primary production (NPP) increased over a 20-year
period at both HOT and BATS at a rate of nearly 2 per cent per year. By contrast, Behrenfield \textit{et al.} [69], using remotely sensed observations, recorded a strong coupling between climate variability and NPP as a result of enhanced stratification of the surface layers of the ocean during periods of increased temperatures. Reductions of NPP, which occur during positive deviations to the stratification anomaly, are attributed to a reduction in the transfer of nutrients from the deep ocean to surface waters. Similar trends between variability in sea surface temperature and primary production have been shown over a 7-year period for all provinces of the Atlantic Ocean traversed by the AMT programme [33], and Polovina \textit{et al.} [70] show for a 9-year period that the spatial extents of the north and south oligotrophic gyres of both Atlantic and Pacific Oceans have increased by 1–4\% per year. It would seem that methodological approach may play some role in the contrasting findings of these different studies [68], for which Saba \textit{et al.} [68] suggest the need for ‘an integrated, multifaceted ocean observing system that incorporates both \textit{in situ} observations and satellite remote sensing in tandem’.

The oceans are a large sink for atmospheric carbon dioxide [34], which is supported through a combination of primary production and particle sinking (the biological pump) [36] and ocean circulation and mixing (the solubility pump). Climate change will tend to suppress ocean carbon uptake through reductions in CO$_2$ solubility, suppression of vertical mixing by thermal stratification and decreases in surface salinity. It is envisaged that climate-driven changes in any of these physical mechanisms will have a subsequent impact on phytoplankton and their ability to draw carbon from the atmosphere into the ocean. This will increase the fraction of anthropogenic CO$_2$ emissions that remain in the atmosphere this century and produce a positive feedback on climate change.

\textbf{(b) Ocean acidification}

The oceans and atmosphere are intimately linked, so that changes to the partial pressure of atmospheric CO$_2$ (pCO$_2$) result in proportional changes in dissolved CO$_2$ in the marine environment. As a result of this, the rise of global temperatures has been buffered by the exchange of approximately 25 per cent of anthropogenic CO$_2$ into the oceans, and it is this condition that has resulted in a profound change to ocean carbonate chemistry and the phenomenon of ocean acidification (OA) [6]. As a consequence, oceanic pH is on average approximately 0.1 units lower than it was prior to the industrial revolution, and future pH levels are predicted to decrease by an additional 0.2–0.3 units over the twenty-first century with recent predictions of anthropogenic CO$_2$ emissions [11]. In addition to decreasing pH, the saturation state of calcium carbonate is lowered, which has implications for organisms that use calcite in the formation of shells and skeletons. Current evidence indicates that large and rapid changes to ocean pH will have adverse effects on a range of marine organisms, with calcifying organisms (which include benthic and pelagic communities) likely to be the most susceptible. While it is recognized that the fixation of carbon into organic and inorganic material through photosynthesis and calcification, respectively, has been shown to be sensitive to increasing pCO$_2$ [11,12], there is ambiguous evidence over the magnitude and even the direction (increase or decrease) in which this will occur [37]. Elevated oceanic pCO$_2$ and the subsequent decrease in pH will have direct and indirect impacts on

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microbial nutrient cycling and carbon fixation, which may fundamentally alter biogeochemical cycles. Current opinion and biogeochemical models assume that phytoplankton and prokaryotic growth is limited in part by nutrient availability (e.g. nitrogen, phosphorus and iron), and that carbon fixation and export are tightly coupled to these nutrient cycles through elemental stoichiometries. Under predicted OA scenarios, microbial activity and hence the biogeochemical cycles they drive may come under pressure from direct and indirect means. Predicting the response of ecosystems and resources is problematic owing to the range of effects of high CO2/low pH reported, the complexity of the whole system, some conflicting experimental results and the unknown effects of acclimatization and adaptation.

Early research efforts into the impact of OA on biogeochemical cycles were largely centred around the fixation of organic and inorganic carbon. Data that describe the impacts of OA on other key microbially driven ecosystem processes, such as nitrogen cycling, are still sparse. A small number of studies have indicated that nitrogen fixation may show a positive response to decreasing pH (e.g. [71]) and this may result in a negative feedback to OA. However, most of these studies have been performed under laboratory conditions on *Trichodesmium*, a single diazotroph species whose response is unlikely to be representative of other nitrogen-fixing groups under natural conditions. Similarly, our understanding of the impact of OA on nitrification is based on a small number of investigations. Current evidence indicates that OA is inhibitory to pelagic nitrification (e.g. [72]), which may result in changes in the NH$_4^+$ : NO$_3^-$ ratio and a decrease in the ocean N$_2$O source. The implications for change to biochemical function due to increasing OA are apparent, but the uncertainty over expected conditions is compounded by the added influence of increasing temperatures and, for some areas, decreasing oxygen levels.

(c) Ocean deoxygenation

The deoxygenation of oceanic waters occurs naturally in oxygen minimum zones (OMZ), deep basins, eastern boundary upwelling systems and fjords [3], but climate-driven changes as described in earlier sections are resulting in the expansion of OMZs in the North Pacific and tropical and sub-tropical areas [5]. Low subsurface oxygen concentrations (hypoxia) exist owing to a combination of weak ventilation that may occur in concert with or independently of organic matter remineralization [61]. Ocean deoxygenation is occurring as the ocean warms and the solubility of dissolved gases decreases, so that the magnitude and volume of OMZs is increasing, with current predictions indicating declines in the global ocean O$_2$ content of 1–7% over the next century [73]. The outgassing of O$_2$ from the ocean to the atmosphere due to climate change could be up to 125 Tmol yr$^{-1}$ by 2100 as a result of the combined effects of increased temperature and enhanced stratification, the thermal effect being responsible for approximately 25 per cent of the overall change [74].

The concentration of dissolved oxygen controls the biogeochemical cycles of carbon, nitrogen and other elements, and dictates the presence or absence of macro-organisms. It therefore plays an important controlling factor in the functioning of ecosystems. Low-oxygen waters are often classed as hypoxic (1–30% O$_2$), suboxic (less than 1% O$_2$) or anoxic (zero O$_2$). The OMZs associated

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with eastern boundary upwellings are characterized by high productivity, though each is distinct in its biogeochemical character and oxygen inventory. Those in the Pacific and Arabian Sea are largely considered suboxic, while those on the eastern Atlantic are hypoxic. This impacts the cycling of elements in intermediate-depth water masses, but, in particular, the oxygen content plays a significant controlling factor on the nitrogen biogeochemistry. Under suboxic to anoxic conditions, denitrification and annamox are likely to be active processes that act as a sink to fixed nitrogen (\(\text{NO}_3^-\) and \(\text{NH}_4^+\), respectively) and thus modify the degree of availability to phytoplankton in surface waters. Under these conditions, denitrification may contribute a source of \(\text{NO}_2^-\) and \(\text{N}_2\text{O}\) and thus increase the oceanic source of this effective greenhouse gas and ozone destroyer to the atmosphere. Regions of suboxia are generally seen to be strong net producers of \(\text{N}_2\text{O}\) [75]. Nitrification, an aerobic process, releases \(\text{N}_2\text{O}\) as waters become increasingly hypoxic, while denitrification can act as either a source or sink under suboxic conditions. There is a subtle balance in the degree of oxygen present that dictates the net release of \(\text{N}_2\text{O}\) during denitrification and nitrification, which makes changes to ocean oxygen content significant. Model predictions indicate that not only are biogeochemical cycles sensitive to small changes in ocean oxygen content but also is the spatial extent of hypoxia [76] and that this response is maximal in suboxic zones. Deutsch et al. [76] describe a direct control imparted by climate change on the variability of low-oxygen zones, which also results in large fluctuations in denitrification and therefore a direct link between climate oscillations and nitrogen limitation of primary productivity. The balance in oxygen content may also impact other microbial processes, and the distribution of higher trophic levels, as lethal and sub-lethal thresholds vary greatly among marine organisms. This may offer a further feedback to atmospheric chemistry, as these areas are key regions in the budgets of other climatic gases, including \(\text{CO}_2\), \(\text{CH}_4\) and halogenated carbon compounds.

\((d)\) Eutrophication and coastal hypoxia

Enhanced nutrient deposition to coastal waters, through fossil fuel burning, fertilizer run-off and waste-water generation, has occurred on a global scale during the industrial age. It is widely accepted that activities such as these have more than doubled the global rate of terrestrial nitrogen fixation, with even higher rates predicted for coming decades [77]. The obvious evidence of this is an increase in primary productivity and algal biomass in coastal waters, though it is the consumption of dissolved oxygen during microbial decomposition of this and other organic material that presents the greatest cause for concern [78]. Under severe conditions of oxygen depletion, the so-called dead zones are created, wherein there exists an absence or significant reduction in the presence of expected macrofaunal communities. Often, these dead zones are associated with stratified, semi-enclosed environments that have restricted water exchange, such as areas within the Black Sea, the Gulf of Mexico and East China Sea, among others. The occurrence of this phenomenon has increased dramatically since the mid-twentieth century, when the use of industrially produced fertilizer began increasing on a massive scale. In 2008, there were reported to be dead zones associated with more than 400 coastal systems that affected an area of greater than 245,000 km\(^2\) [78]. As described already, the depletion of oxygen can affect

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not only the benthic faunal communities, but also the biogeochemical cycles inherent to these systems. The death or migration of bioturbating animals that ventilate sediments and influence porewater chemistry may have knock-on effects to rates of nitrification and denitrification, in addition to those associated with the direct effect of decreasing oxygen levels. As denitrifying organisms obtain oxygen from $\text{NO}_3^{-}$ under decreasing suboxia, there is a subsequent reduction of fixed nitrogen and potential for increased $\text{N}_2\text{O}$ production. Under anoxic conditions, toxic hydrogen sulfide is produced, while the remineralization of organic matter that has contributed to the hypoxic conditions also produces $\text{CO}_2$, so that there exists a coupled OA and deoxygenation scenario that, in the warmer climate of tomorrow, introduces a whole matrix of synergistic stressors on the marine ecosystem [7,61].

4. The ongoing challenge

While it is apparent that a reduction in greenhouse gas emissions is essential in order to minimize future levels of ocean acidification, warming and deoxygenation, we are already committed to experience a certain degree of each [7,79]. There is therefore an urgent need to reconcile our current understanding of biogeochemical cycles with changes forced by anthropogenic activity. Specifically, during the next two decades or so, there will be an emphasis on the determination of individual and synergistic or antagonistic impacts of these stressors in order to inform prediction and mitigation strategies.

We are therefore charged as a research community with the challenge to determine the sensitivity of the ocean to the external forces acting upon it and to the role that ocean biogeochemistry will play in alleviating (or exacerbating) the impact of change on the Earth system and human society. To deliver this, there is an ever-pressing need to fully integrate ocean biogeochemistry with Earth system science by employing a comprehensive multidisciplinary approach. The engagement across disciplines that include atmosphere, climate and physical oceanography must necessarily link to the social and economic sciences in order to create an effective dialogue between research and decision-making communities.

Boyd et al. [80] reviewed a series of laboratory, shipboard and field experiments in order to comment on the design features of the experimental approach to be taken when investigating the impact of climate change on oceanic phytoplankton. A number of phytoplankton-group-specific limiting factors were noted, which led to synergistic and antagonistic impacts on productivity or community structure. Elevations in temperature and iron were shown to synergistically increase the growth rate of Antarctic diatoms, while an antagonistic relationship was observed between iron and light on the growth of $\text{Phaeocystis antarctica}$. Boyd et al. [80] recommended that, in order to improve on existing approaches, it is necessary to ensure the consideration of all environmental factors that are likely to be impacted, and the interactions between them. Factorial matrix perturbation experiments should be used to investigate subsets of conditions that are relevant to specific phytoplankton groups. Further to improving the observational and experimental approach is the requirement to incorporate the capability of DGOMs [58] and other state-of-the-art ecosystem models [81] that are capable of
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resolving and predicting marine ecosystem function under actual or theoretical climate change scenarios. From a biogeochemical perspective, the over-arching question to be asked is huge: How will anthropogenic forced change, coupled with natural climatic variability, affect biogeochemical functioning of the marine ecosystem, from cellular process to ecosystem level, and how will such changes feed back to the Earth system?

Even today, after more than a century of observational oceanography, it is a widely held belief that the oceans are grossly undersampled [61]. Therefore, a fundamental approach to address this is to significantly increase the spatial and temporal extent of oceanographic and, from this paper’s perspective, biogeochemical observations. This will enable us to determine the variability of natural processes, and their sensitivity to changes in the environment, and to detect and resolve the enigmatic decadal (and longer) trends in ocean character. The most obvious example of a concerted effort of increasing coordinated observations that is currently operational is the Global Ocean Observing System (GOOS; http://gosic.org/ios/goos). GOOS is a global system for sustained observations of chemical and physical variables in the ocean, which, together with the Global Climate Observing System and the Global Terrestrial Observing System, forms the Global Earth Observing System of Systems. GOOS maintains a permanent system for observation, modelling and analysis of temperature, salinity and, to a lesser extent, other variables, which include CO₂ and O₂. In addition to ship-based observations, data sources include remote sensing, moored instruments and free-floating and profiling floats such as those used in the ARGO programme. ARGO involves 23 countries and, as of January 2012, has been responsible for the deployment of 3476 autonomous floats throughout the oceans. These free-drifting profiling floats measure the temperature and salinity of the upper 2000 m of the ocean and regularly transmit data, so that data are publicly available within hours of collection. A limited number of ARGO floats and similar profiling bodies have been exploited to carry additional sensor packages. These include transmissometers to estimate particulate organic carbon (POC) and carbon export [82,83], bio-optical sensors to determine chlorophyll-a concentrations [83] and nitrate sensors [84]. The combination of these sensors, if deployed on a sufficient number of floats, will provide a means to improve validation of remotely sensed ocean colour products, which include chlorophyll, phytoplankton carbon and improved bio-optical models of primary production. One adaptation of such floats, Carbon Explorers, have been successfully used to determine POC and particulate inorganic carbon fluxes and have the potential to be further developed to determine the full extent of the carbon inventory [85]. A further development from profiling floats are autonomous underwater vehicles or gliders that can carry a suite of sensors and, being propeller-driven, can be used to deliver high-resolution surveys or longer transect-type studies. Vehicles such as these are now being used to deliver high-resolution information on physical, chemical and biological characteristics in a manner not possible from ship-board observations or even through the combined observations of satellites and profiling floats [86,87]. The integration of reliable nutrient (e.g. nitrate, phosphate and iron) sensors with sufficient sensitivity for upper ocean conditions into floats, moorings and autonomous vehicles now seems realistic after several years of low-sensitivity instrumentation. Commercially available packages are now available for moored deployments, which incorporate automated molecular
probes to inform on microbial community composition and its genomic and proteomic activity, such as the Environmental Sample Processor [88]. The next generation of these and other instrumentation packages are necessary to facilitate a large-scale improvement in the extension of the current biogeochemical observational capacity. The continued development of sophisticated, intricate and high-resolution platforms that will improve predictive capacity and the resolution of natural annual and decadal variability is essential to fully augment mechanistic studies of the adaptive capability of ocean biogeochemistry.

It might seem, then, that the oceans are actually well sampled and that there is an existing infrastructure in place to coordinate and output real-time data. In effect, this is only the case for a very restricted set of variables. Future biogeochemical research ought to be directed to extend the process-based studies of the type performed under the auspices of JGOFS and SOLAS to include mechanistic responses of organisms and biogeochemical cycles to the increasing perturbations associated with the ocean stressors identified above. There is then the need to take an Earth system approach to incorporate targeted experimental process studies, as championed by Boyd et al. [80], with large-scale observations using state-of-the-art autonomous instrumentation, which fully embraces the application of the new generation of genomic approaches, integrated models and remote sensing.

5. A role for the UK

The UK has a well-placed extensive experience base to address concerns associated with ocean biogeochemistry. Existing centres, which include universities, government agencies and NERC institutes and collaborative centres, each have independent identities but are well versed in collaborative ventures to provide the multidisciplinary approach required to address burning issues such as those identified here. In 2011, the National Oceanography Centre (NOC) Association (http://noc.ac.uk/about-us/noc-association) was formed and in December of that year produced its publication ‘Setting Course’, which presents the vision to create a more integrated UK marine science community to tackle the environmental challenges ahead. The NOC Association comprises the NERC-funded marine science community of the UK. The vision is to guide UK marine science into the future by the provision of large-scale infrastructure such as ships and underpinning activities such as data management under a nationally coordinated structure, and to place ocean research with atmospheric, polar and terrestrial disciplines alongside living systems, including human society, together in the context of a whole Earth system. The ‘Setting Course’ document calls for a funding environment that ensures the health of our intellectual capital base and stimulates collaborative research that nurtures a varied research environment and facilitates fit-for-purpose national research infrastructure and capability. In a societal environment that is globally economically fragile and politically dynamic, it is difficult to predict funding and organizational structures far into the future, but it is encouraging to be part of a unified approach to future marine research priorities. From a biogeochemical point of view and with respect to previous sections of this paper, the ‘Setting Course’ vision strongly advocates the need to prioritize the understanding of the role of the ocean in the Earth system and on
the human population, on time scales of days to centuries and from local to global space scales. It recognizes fully the significant role of the oceans in regulating climate and the pressures associated with a high-CO$_2$ environment and enhanced nutrient enrichment.

In summary, the UK has indicated its intent to approach this great challenge head-on, and to direct resources with which to do so. In order to do justice to this vision, there are a number of priorities that have been identified within this paper, which should feature in our research agenda:

— maintain a global approach through the sustained involvement in polar to tropical seas, which encourages and facilitates multidisciplinary integration, and which allows the targeting of sensitive ocean areas;
— foster research programmes that are not constrained by short-term (3–5 year) funding, to allow realistic time frames within which to investigate adaptation and acclimatization to changing environments;
— improve confidence in the ability to distinguish natural trends and variability from those forced by anthropogenic activity;
— support the development, maintenance and operation of autonomous instrumentation, which includes biogeochemically relevant sensors, for deployment on a diverse fleet of profiling floats, gliders and moorings;
— increase sustained observations in time and space, and for observations to be closely integrated with targeted measurements of biogeochemical processes, which are supported by model and observational experimental interrogation of relevant change scenarios;
— harness increasing computing power to run model experiments that can direct multi-factorial experimental programmes and inform on appropriate targets for process studies; and
— contribute to the security and continuity of satellite observations and further develop the ability to estimate process rates, particle loads and plankton composition from remote sensing.

It is without doubt that ocean biogeochemistry and the oceans in general are facing increasing pressures from man’s activities and that, even if CO$_2$ emissions and nutrient additions were immediately reduced to pre-industrial levels, there is sufficient inertia in the system to ensure that the effects of warming, ocean acidification, deoxygenation and eutrophication will remain for several decades into the future. The marine research community has wholly embraced these concerns and has been pro-active in the development of research programmes to inform on the degree to which organisms, ecosystems and biogeochemical cycles may be impacted. The importance of the oceans to the well-being of human society is absolute, and it is essential that this message be transferred clearly and effectively to decision- and policy-makers.

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References


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Changing ocean biogeochemistry


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