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Review article

The microbial carbon pump and climate change

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Abstract

The ocean has been a regulator of climate change throughout the history of Earth. One key mechanism is the mediation of the carbon reservoir by refractory dissolved organic carbon (RDOC), which can either be stored in the water column for centuries or released back into the atmosphere as CO_2 depending on the conditions. The RDOC is produced through a myriad of microbial metabolic and ecological processes known as the microbial carbon pump (MCP). Here, we review recent research advances in processes related to the MCP, including the distribution patterns and molecular composition of RDOC, links between the complexity of RDOC compounds and microbial diversity, MCP-driven carbon cycles across time and space, and responses of the MCP to a changing climate. We identify knowledge gaps and future research directions in the role of the MCP, particularly as a key component in integrated approaches combining the mechanisms of the biological and abiotic carbon pumps for ocean negative carbon emissions.

Sections

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Introduction

The ocean represents the largest active carbon reservoir on Earth, harbouring 50 times more carbon than the atmosphere, and therefore plays a critical role in regulating climate change[1,2]. The major components of the ocean carbon reservoir include dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate organic carbon (POC) and particulate inorganic carbon. These carbon pools are mediated by physical, chemical, biological and biogeochemical mechanisms known as the solubility carbon pump (SCP), microbial carbon pump (MCP)[3], biological carbon pump (BCP)[4,5] and carbonate counter pump (CCP)[6] (Fig. 1). The SCP depends on abiotic controls of the partial pressure difference between the atmosphere and the ocean surface, and is the mechanism by which increasing atmospheric CO_2 concentrations lead to ocean acidification[7]. The MCP depends on the microbially mediated physiological and ecological processes transforming DOC from labile (LDOC) to refractory (RDOC) states. The latter can escape biological oxidation and chemical equilibrium, and be sequestered in the water column for decades, centuries or millennia[3]; however, the turnover of RDOC is under debate[8]. The BCP is based on carbon fixation by phytoplankton in the surface ocean and the subsequent export of organic carbon to the ocean interior and seabed. The BCP has been studied for about half a century[9–12]; therefore, only the part that is intertwined with the MCP is addressed in this Review. The CCP is based on the precipitation of carbonate by calcifying organisms that release CO_2:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad (1)$$

and thus, it is called a counter pump. The proportion of the produced CO_2 that is released to the atmosphere depends on the chemical, biological and physical conditions of the water, and thus needs to be addressed in the context of an ecosystem and from the perspective of interactions between the MCP, BCP, CCP and SCP.

Knowledge of the interactions between the MCP, BCP, CCP and SCP is important for a better understanding of the controlling mechanisms of carbon sequestration in the forms of POC, particulate inorganic carbon and RDOC in the ocean. RDOC is an enigmatic part of the ocean carbon reservoir and plays a unique role in the regulation of carbon cycling and climate change from a long-term dynamic perspective. It is often less appreciated that the delicate balance between ocean total DIC and total alkalinity can be easily shifted by seemingly small changes mediated by the MCP, and this has been of critical importance in regulating climate change over the millennia of the history of Earth[13]. If only 0.5% of DIC is converted to RDOC, it could result in a decrease of 25 parts per million (ppm) in the partial pressure of CO_2 (pCO_2) at the sea surface and in the atmosphere, which is about 28% of the CO_2 change between glacial and interglacial times, or equivalent to 12 years of cumulative pCO_2 change owing to anthropogenic carbon release around the world today[13,14]. In this context, assessment of the MCP is key in determining the production and fate of marine RDOC. In this Review, we explore the characterization of RDOC compounds, their recalcitrance and interactions with microbial diversity, factors influencing their production and distribution, their role in paleoclimate and their response to climate change[15–18]. We also define future research directions needed to fill crucial knowledge gaps and to assess the potential synergistic effects of the combined BCP–CCP–MCP–SCP (BCMS)[19] system to increase the removal of atmospheric CO_2 to achieve ocean negative carbon emissions (ONCE) and thereby mitigate the impacts of climate change.

The MCP

The oceans are full of invisible but globally impactful microorganisms[20]. They are the main bearers of biomass and mediators of energy flux in the marine ecosystem, assuming a pivotal role in biogeochemical cycles. Despite substantial advances in our understanding of the functioning of marine microorganisms, several enigmas remain. DOC accounts for more than 90% of the total marine organic carbon pool[21] and serves as the energy and carbon source of heterotrophic microorganisms supporting the microbial loop[22]. Thus, how can a huge reservoir of DOC remain despite the myriad of hungry microorganisms? This situation has puzzled microbiologists long before the concept of the MCP[3] emerged a decade ago. The MCP refers to the microbial transformation of organic carbon from labile to refractory states, that is, to RDOC that resists further utilization, although the turnover time of RDOC components is still not known. RDOC can remain in the water for a long time, leading to accumulation and maintenance of the large marine DOC pool to approximately 642 Pg of carbon[23], almost equivalent to the total carbon inventory of atmospheric CO_2.

A critical step in moving from a conceptual framework to a recognized theory is through experimental studies to prove that RDOC is produced via the MCP. One piece of evidence came from the Aquatron mesocosm experimental study performed at Dalhousie University in Canada using a tower tank containing around 117,100 litres of water. In the experiment, RDOC with a fingerprint (as determined by Fourier transform ion cyclotron resonance mass spectrometry) similar to that of oceanic water from 2,000 m depth was produced from LDOC during the incubation[24]. Several key microbial pathways related to the production of RDOC were identified via metagenomic analysis in the Aquatron experiment[25]. Even if the ratio of RDOC production to LDOC consumed is minimal, RDOC can accumulate over time and become a large carbon pool. However, it remains challenging to untangle the internal cycling because there is no direct evidence reported to date to indicate that the DOC pool in the deep ocean is increasing yet fluctuations in the RDOC pool must exist throughout the history of Earth[26,27].

The MCP involves heterotrophic, autotrophic and viral activities, including decomposition and degradation, synthesis and conversion, and lytic processes[3,28,29]. These MCP processes are successive and dynamic under changing environmental conditions. The products of the MCP, namely RDOC compounds, are differentiated into RDOCt and RDOCc fractions[30]. RDOCt is defined as the fraction that is intrinsically recalcitrant in a given environmental context, whilst RDOCc is composed of diverse molecules with varying concentrations but which are below their respective thresholds for efficient uptake[30]. The differentiation between RDOCt and RDOCc provoked a debate on 'recalcitrance' or the 'dilution hypothesis'[31–34], which further led to the quantification of RDOCt and RDOCc. Eventually, RDOCt was shown to be the major component of RDOC[33,35].

There are fundamental differences between the MCP and other carbon pumps. For example, the BCP occurs through photosynthetic production of organic particles and their sedimentation from the surface to the seabed whilst the MCP does not depend on such physical transport processes. The MCP theory suggests that high levels of photoautotrophic carbon fixation do not necessarily correlate with high levels of carbon sequestration[36]. Thus, the most productive waters are often carbon sources to the atmosphere rather than sinks[37,38]. The MCP also changes the elemental composition of organic matter in the ocean, affecting the ratio of carbon to nitrogen to phosphorus by depleting nitrogen and phosphorus in the dissolved organic matter (DOM) pool while retaining carbon (3511:202:1)[3,39], which is far from

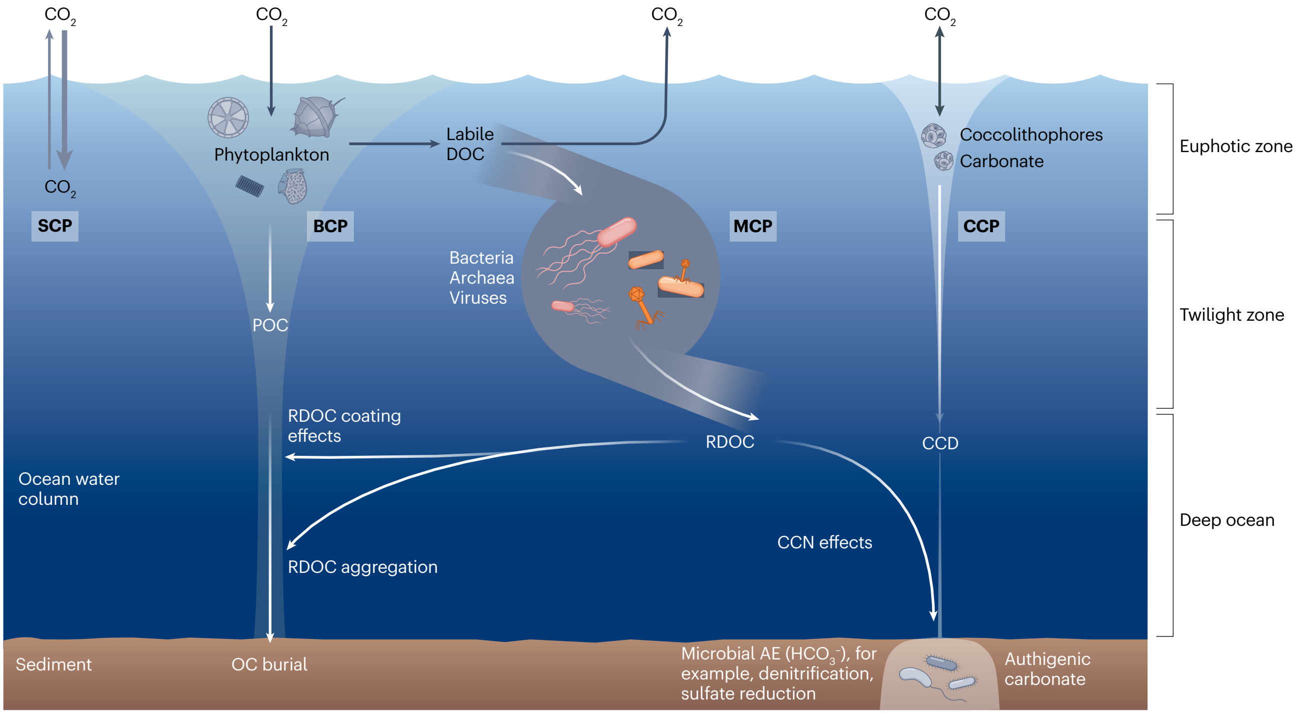

Fig. 1 | Marine carbon cycling and the major processes and mechanisms involved. The solubility carbon pump (SCP) is driven by the difference of CO_2 partial pressures between the atmosphere and surface waters; exchanges of CO_2 occur through dissolution into water or release into the air. Generally, the SCP refers to the pumping of CO_2 from the atmosphere into the ocean driven by abiotic processes such as lowering temperature and downward mixing. The biological carbon pump (BCP) refers to a series of biogeochemical processes that transport organic carbon (mainly particulate organic carbon (POC)) from the surface to the ocean interior. The BCP flux depends on sinking processes and attenuates sharply with depth. Only a tiny portion of the carbon fixed in the euphotic zone reaches the bottom of the sea for long-term carbon sequestration. The microbial carbon pump (MCP) refers to a series of microbial physiological and ecological processes that transform labile dissolved organic carbon (DOC) to refractory DOC (RDOC), which can stay in the water column for a long time (up to thousands of years), serving as a carbon sequestration mechanism. The MCP occurs throughout the ocean water column. The carbonate counter pump (CCP) refers to the processes of formation and deposition of carbonate. Because of the accompanied CO_2 release during the formation process of carbonate, it is called a 'counter' pump. However, the release of CO_2 in the real world is not really at equivalent levels to those indicated in the chemical equation (see Equation 1 in the main text). On the continental shelf, the CCP can constitute long-term carbon sequestration if the precipitated carbonates are buried in the sediment. In oceanic waters, carbonates precipitate at the surface water (mainly by microalgae such as coccolithophorids) but dissolve at the carbonate compensation depth (CCD) layer. In the sediment, authigenic carbonate occurs when alkalinity increases by microbial processes (see the main text). The RDOC coating effect refers to the processes by which the RDOC molecules adhere to POC particles, to a certain degree preventing further degradation of POC. AE, alkalinity enhancement; CCN, carbonate condensation nucleus; OC, organic carbon.

the Redfield ratio (106:16:1) for phytoplankton biomass. By releasing nitrogen and phosphorus while preserving carbon, the MCP facilitates nutrient recycling for primary production and carbon sequestration and raises questions about the composition of RDOC, its long-term stability and its sources. It seems that deep ocean carbon fixation by chemolithotrophs plays a substantial role in DOC production[40] but, to the best of our knowledge, no data to date demonstrate how much RDOC is produced by chemolithotrophs.

The nature of RDOC

RDOC was defined based on its bioavailability and turnover time[3,41], with the age of RDOC inferred from radiocarbon dating of the bulk or broadly defined fractions[42–44]. However, deep ocean sources of ^{14}C-free DOM have been found in recent years, suggesting potential biases in this dating method[44,45]. These studies challenged the conventional view that RDOC is evenly distributed in concentration and radiocarbon age throughout the ocean. Instead, the data indicate that both the concentration and radiocarbon age of RDOC vary depending on depth and location[46]. The new evidence challenges our knowledge of deep ocean RDOC age and, therefore, assessment of the functioning of MCP may be a more promising route to determining the production and fate of RDOC.

Characterization of the composition of RDOC has improved substantially over the past decade with the development of instrumentation and techniques[23,24,47]. The composition of RDOC can be defined by its molecular optical properties, which can be detected by ultraviolet-visible and fluorescence spectroscopy. The marine fluorophores, which mimic the fluorescent signals of humic substances in DOM ($FDOM_H$) in freshwater systems, were found in the products of marine autotrophic and heterotrophic organisms[48–50]. Given the residence time of terrestrial $FDOM_H$ and the constancy of marine $FDOM_H$ in the deep ocean, microorganisms contribute substantially to marine $FDOM_H$ (refs. 51–53). $FDOM_H$ is a proxy of RDOCt as DOM fluorescence increases with the microbial transformation of organic substrates[51,52,54].

The application of ultra-high-resolution mass spectrometry in bulk DOM analyses unveiled the mystery of unknown complex DOM compounds. A diverse group of carboxyl-rich alicyclic molecules (CRAMs) account for a substantial fraction of the RDOC in the deep ocean[55–58]. They have been shown to accumulate during microbial transformation processes as evidenced by laboratory experiments[59], environmental surveys[60,61], incubation assays[62] and metagenomic analyses[25]; they are therefore another proxy of RDOC. However, limitations of the detection and extraction methodologies mean that CRAMs describe only part of the complexity of RDOC. It is also important to note that not all CRAMs can be simply classified as RDOC[63,64]. A large fraction of the refractory compounds and molecules remains unknown even in the accessible data sets.

Dissolved black carbon (DBC) also forms part of the biologically recalcitrant components in the ocean[65–67]. The major sources of DBC are land-based biomass burning and fossil fuel combustion, and this DBC is then transported to the ocean via rivers and atmospheric deposition[68,69]. However, recent evidence from isotope studies suggests that DBC has biological sources[70]. DBC is also derived from marine hydrothermal vents and methane seeps[71,72]. Given that the DBC pool in the global ocean is 9.5–14 Pg of carbon and that its ^{14}C age is about 23,000 years[73], its contribution to RDOC in terms of quantity and age appears insignificant (estimated to be 1–2% and 4–8%, respectively).

Microbial production and transformation of RDOC

The generation of RDOC by the MCP involves a series of sequential microbial processes[30]. Different microbial groups exhibit distinct capabilities in organic matter degradation. Certain microorganisms assimilate organic matter released by other microbial taxa, whilst specific RDOC compounds are uniquely associated with particular microorganisms[74,75].

Recent investigations into the key species participating in RDOC production and transformation underscore the intricate mechanisms through which microbial activities convert labile DOM into a refractory state[75].

Enzymatic oxidation and hydrolysis are key processes in the microbial degradation of DOM. Studies on enzyme diversity, the substrate specificity of enzymes (functional recalcitrance may arise from the requirement for specialized enzymes), enzymatic kinetics (reaction rates and substrate affinity) and cellular allocation of enzymes in kinetic metabolic networks[76–79] have demonstrated the complexity and diversity of microbial functions in transforming DOM, thereby influencing the composition and distribution of in situ DOM composition. Several bacterial groups have been associated with the production of RDOC, including members of the *Flavobacteriaceae*, *Polaribacter*, *Roseobacter*, *Alteromonas* and *Pseudomonas* families[75,80].

The addition of various DOM sources to bioassays, such as simple compounds or polymers[81], phytoplankton-derived DOM[58,82], and soil or sediment DOM[54], led to the formation of chemically recalcitrant components (for example, CRAMs). Picocyanobacteria, one of the major groups of primary producers in the global ocean, produce typical deep ocean $FDOM_H$ components from degradation products of photosynthetic phycobilin pigments[48]. The microbial degradation of carotenoids[83] is widely found in a variety of algae and bacteria, resulting in the production of CRAMs[84], and several bacterial groups, such as the SAR202 clade and the *Piscirickettsiaceae*, *Hyphomonadaceae* and *Alcanivoracaceae* families, have demonstrated variable degradation rates for certain CRAM substrates[76–79].

Linking diverse microorganisms to complex RDOC matter

The advent of advanced analytical tools, such as Fourier transform ion cyclotron resonance mass spectrometry and nuclear magnetic resonance after solid-phase extraction by modified styrene-divinylbenzene polymer resins, has greatly improved our understanding of the diversity and complexity of DOM, both in terms of chemical composition and compound structure[55,64]. At the same time, with the development of omics approaches, our understanding of the diversity of microbial communities has expanded from the taxonomic level to genetic and metabolic functions. Recent studies have begun to address the challenge of linking the interactions between chemical and microbial complexity (Fig. 2).

Microorganism–DOM molecular network analyses are important statistical tools to visualize the complex interactions between diverse microbial communities and DOM compounds[85,86]. Network graphics not only visualize the complexity of these interactions but also provide a comprehensive picture of how the intricacy varies temporally and spatially[86]. The key microbial species involved in RDOC formation and distribution patterns have been identified based on these analyses, along with the roles of specific microbial groups in the formation and transformation of DOM, and their responses to environmental changes. For example, Gammaproteobacteria, Betaproteobacteria, *Cytophaga*, Thaumarchaeota and Euryarchaeota were found to contribute to the consumption and decomposition of phytoplankton-derived DOM[74,87,88].

Long-term dynamics observations at coastal time-series stations have revealed that fluctuations in the environment and DOM are determining the structure of microbial communities[89]. DOM components, such as CRAMs, D-amino acids, highly unsaturated aromatic compounds and nitrogen-rich compounds, were recognized by these correlation networks, indicating the linkage between the recalcitrance of DOM and specific microbial species[25,90]. Chemically recalcitrant compounds also frequently co-occurred with key microbial species along latitudinal transects and other environmental gradients[85].

Drivers of RDOC distribution in a changing ocean

Terrestrial versus indigenous DOC

The MCP also exists in terrestrial soil environments and is therefore referred to as the soil MCP[15]. Once the soil RDOC is washed into aquatic environments, it is subject to new biogeochemical challenges, although some of it remains as $FDOM_H$. In coastal waters, most organic matter is labile and RDOC mainly consists of RDOCt[30]. Terrestrial $FDOM_H$ may remain refractory until it is discharged into the ocean, where it is subject to further decomposition by the marine microbial community. However, in coastal regions, specifically when high nutrient concentrations stimulate algal blooms (a condition known as eutrophication), mostly LDOC is produced, which is then efficiently consumed by heterotrophic microorganisms. This locally produced LDOC has a priming effect[91,92] on the river-discharged terrestrial RDOC, remobilizing the latter, at least partly, for microbial utilization. Enhanced photochemical degradation of terrigenous DOM in the coastal ocean also produces labile DOM. Thus, productive estuarine and coastal waters are often sources, rather than sinks, of atmospheric CO_2 (refs. 93,94). Therefore, reducing eutrophication has been proposed as an approach to enhance carbon sequestration in coastal waters[38,92]. This suggestion is supported by experimental results in estuarine and offshore waters[95–97].

Influence of environmental conditions on microbial activity in the ocean water column

Microbial transformation of DOM varies across various environmental gradients such as oxygen, temperature and nutrients[98]. The chemical composition of DOM also varies with ocean depth[56,99] (Fig. 3).

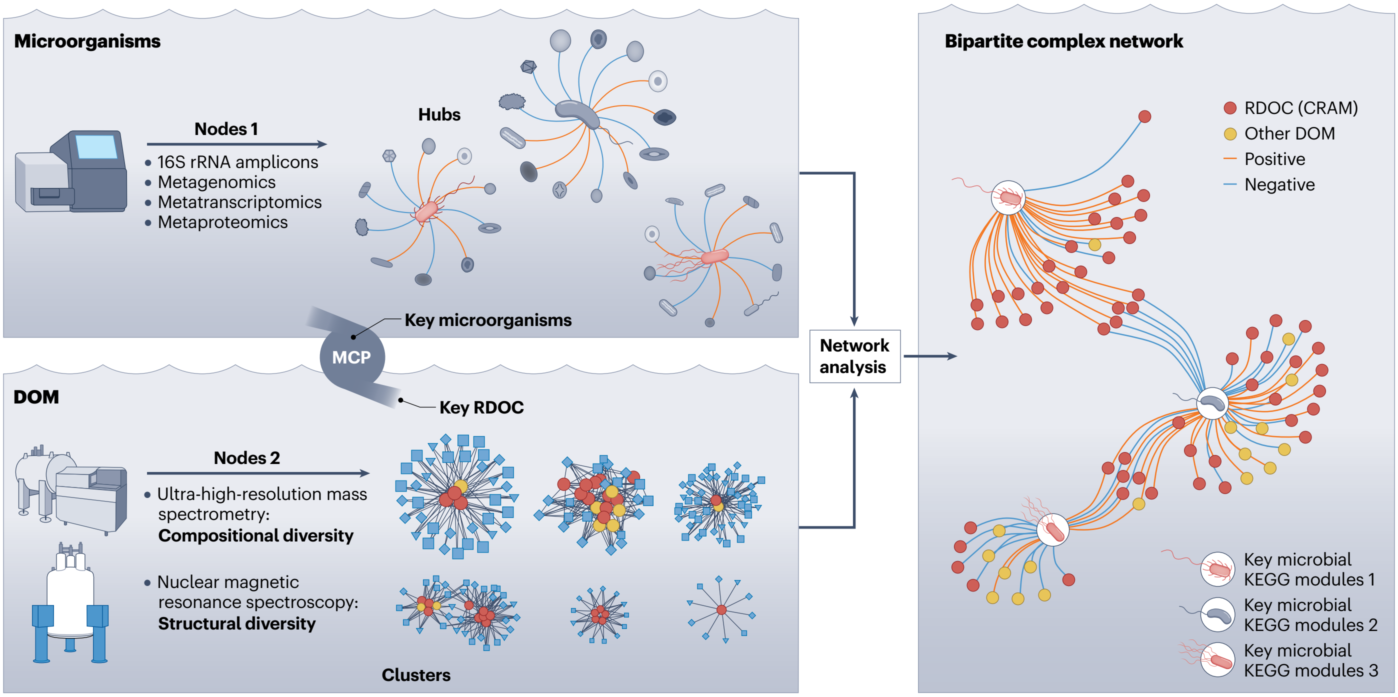

Fig. 2 | Microorganism–DOM complex networks. Microorganism–dissolved organic matter (DOM) complex networks contain two types of nodes: the microbial nodes and the DOM nodes. Connections are made between nodes based on correlations of data sets. Microbial diversity can be analysed with 16S rRNA amplicons, metagenomics, metatranscriptomics and metaproteomics. As for the DOM components, ultra-high-resolution mass spectrometry can be used to determine compositional diversity and nuclear magnetic resonance spectroscopy can be used to reveal structural diversity. These individual connections collectively form the overall network pattern. Analysis based on key nodes unveils the relationships between refractory dissolved organic carbon (RDOC) molecules (for example, carboxyl-rich alicyclic molecules (CRAMs)) and key microbial populations (for example, Kyoto encyclopaedia of genes and genomes (KEGG) modules, including metabolic pathways, signalling pathways, complexes and functional set), thus revealing the connections between them. Red lines represent positive associations and blue lines represent negative associations between RDOC molecules and microbial populations (right). MCP, microbial carbon pump. Adapted with permission from ref. 25, Elsevier, and from ref. 74, CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

Water column stratification leads to variations in temperature, dissolved oxygen and pH, resulting in the accumulation of RDOC in the water column[100]. At elevated temperatures, heterotrophic respiration is enhanced, and the efficiency of organic carbon utilization and transformation increases. Availability of dissolved oxygen also has a significant impact on the preservation and degradation of DOM molecules[101,102]. In oxygen minimum zones, microbial degradation of DOM is reduced[103] and sulfur-containing compounds are formed, facilitating RDOC production[104,105]. Therefore, in these regions, carbon sequestration is relatively more dependent on the fractionation of RDOC[106] compared to aerated water columns, where POC export is dominant.

In the deep ocean, chemoautotrophic processes fix DIC, providing DOC sources other than those derived from the decomposition of sinking particles[107]. A recent study on the effect of hydrostatic pressure[108] indicates the presence of a fraction of deep-sea DOC that is not utilized owing to the combined effect of high hydrostatic pressure and low temperature. Low temperature and high hydrostatic pressure result in higher activation energy requirements for microbial enzyme synthesis and reduced growth compared to depressurized conditions. The addition and removal of deep-sea RDOC is also driven by abiotic processes, such as hydrographic processes[109], and by high temperature in hydrothermal vent systems[110–112].

Beneath the ocean

Aggregation processes in the ocean produce refractory POC in addition to RDOC-coated POC, which is more resistant to decomposition and thus transported down to the sediment for long-term storage[30]. Refractory POC and RDOC in the sediment will undergo a series of chemical reactions under high pressure and temperature (for example, pyrolysis), which over time could produce polycyclic aromatic hydrocarbons[113,114]. These compounds, in turn, would form a solid material of high molecular weight that is the precursor to kerogen[114] — the initial stage in the formation of fossil fuels. Once this hypothetical sequence of processes is experimentally tested, we will be able to bridge the gap between marine organic matter from the water column and kerogen in the Earth's crust.

The MCP and climate change

Climate change will alter oceanic conditions, which may influence the efficiency and capacity of the MCP and other carbon pumps to sequester carbon, potentially altering its role in climate regulation. Anthropogenic CO_2 emissions from fossil fuel use, deforestation and cement production, among others, have increased atmospheric CO_2 from 280 ppm in pre-industrial times to approximately 420 ppm in 2023 (according to the Global Monitoring Laboratory). There is consensus in the scientific community[115,116] that emission reductions alone are insufficient and too

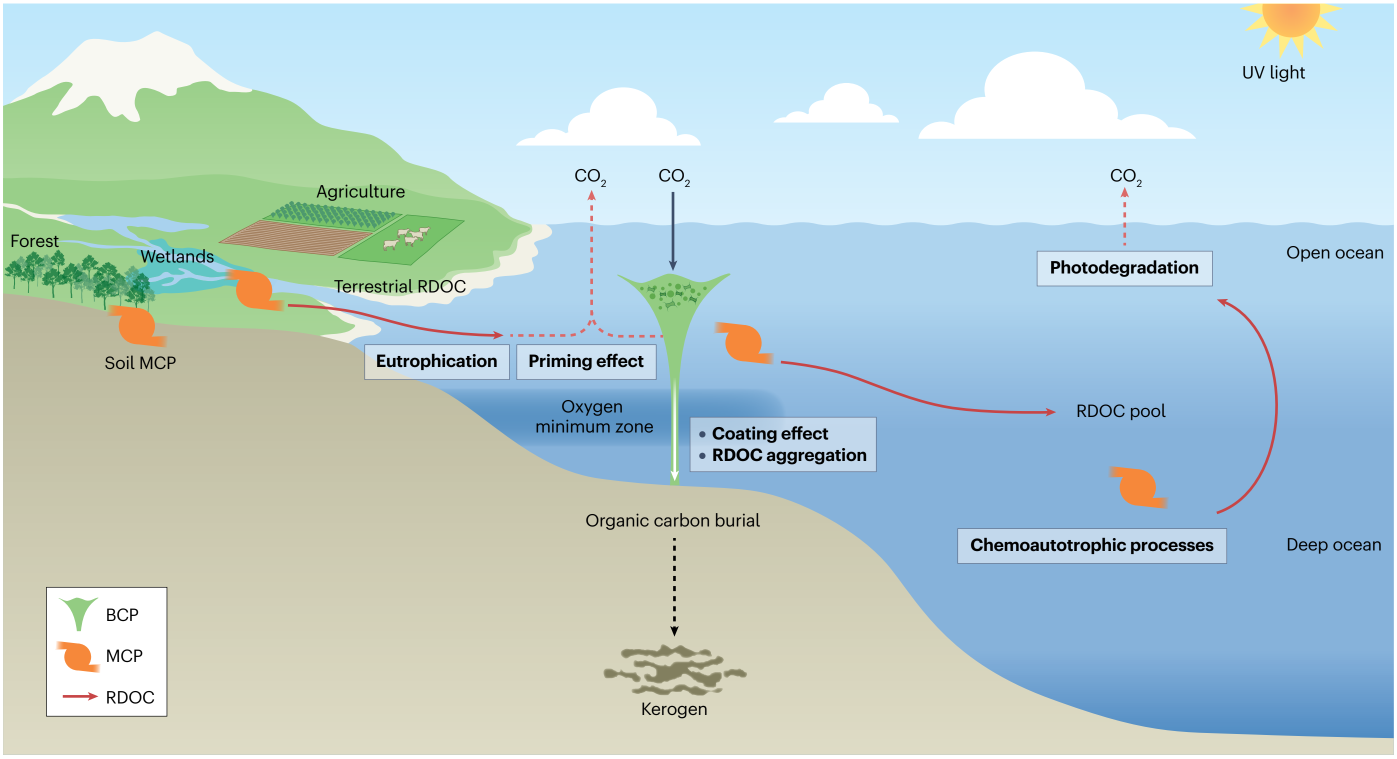

Fig. 3 | The MCP in changing environments. Microbial carbon pump (MCP) processes (orange) occur in environments from soil to seawater and from coastal to oceanic waters. Changes in environmental conditions, such as nutrients and dissolved oxygen concentrations, have impacts on the production and transformation of refractory dissolved organic carbon (RDOC) (red arrows). For example, eutrophication could ultimately lead to a reduction in the efficiency of the MCP. This can occur because heterotrophic microorganisms are fuelled by indigenous labile organic carbon, together with high nutrients; therefore, they become not only larger in population but also more energetic and capable of respiration, and some terrestrial RDOC compounds become no more refractory in the presence of these microorganisms. Such priming effects lead to high rates of biodecomposition and subsequent photochemical degradation. The biological carbon pump (BCP), depicted by the green funnel-shaped icon, involves CO_2 absorption by phytoplankton via photosynthesis, and subsequent organic matter generation within the food web. This organic matter partly feeds into the MCP. RDOC in oceanic surface seawater is subject to photodegradation. Chemoautotrophic processes that occur in the deep ocean, such as the conversion of ammonia to nitrate by nitrifying bacteria in the deep sea and the oxidation of hydrogen sulfide by sulfur-oxidizing bacteria at hydrothermal vents, are crucial for energy conversion in light-independent ecosystems and elemental biogeochemical cycling. Microorganisms involved in these chemoautotrophic processes could also contribute to the RDOC pool. RDOC can aggregate, contributing to particulate organic carbon burial in the sediment, and could be associated with the formation of kerogen, which is the source of oil. The dotted black lines represent inert organic matter in sediments that would then form a high-molecular-weight solid material, which serves as the precursor to kerogen (see the section 'Beneath the ocean').

slow to avoid a global warming catastrophe. Thus, ONCE approaches or CO_2 removal technologies are needed to remove significant (more than 10 gigatonnes per year) atmospheric CO_2 to limit global warming to 2 °C or, preferably, 1.5 °C above pre-industrial temperatures by the end of this century[1,2]. Towards this goal, the well-known mechanisms of the BCP, CCP and SCP have all been addressed in the literature, but the MCP is rarely discussed in this context. Therefore, we describe the role of the MCP in response to climate change from a historical point of view with implications for current and future situations.

The MCP-driven RDOC pool regulates climate change

The dynamics of the MCP-mediated RDOC reservoir can lead to either carbon sequestration or CO_2 release over geological time scales, suggesting that the MCP is a two-way regulator of climate change (Fig. 4). During interglacial periods of high atmospheric CO_2 concentrations, the oceans experienced increasing warming, stratification and deoxygenation[117]. In such cases, the MCP would have become stronger[118], leading to an increase in RDOC production and accumulation and contributing to the mitigation of global warming. An extreme example is the case of the Cryigenian period of the Neoproterozoic era (720–635 million years before present), where a strong negative shift in the carbon isotopic composition of sedimentary carbonates, together with a generally unchanged carbon isotopic composition of coexisting organic matter[26,119,120], indicates the presence of an unusually large RDOC reservoir at that time and therefore a very effective MCP[27,30,121,122]. The development of this large RDOC reservoir coincided with the extreme glacial event extended to the equator known as 'Snowball Earth', which was widely confirmed in geological records[12,119,123,124]. By contrast, during glacial periods, the formation of sea ice leads to high salinity-driven mixing that brings oxygen to depth and induces increased degradation of RDOCt[125] with consequent CO_2 emission, which in turn mitigates global cooling. During deglaciation, the CO_2 stored in the deep ocean was released into the atmosphere, leading to rapid warming of the global climate[126,127]. There was a rapid increase in atmospheric CO_2 concentrations, accompanied by a significant decline in its $\Delta^{14}C$ (a measure of the age of a sample containing organic materials by using the properties of radioactive carbon, which decays at a known rate), suggesting that the CO_2 entering the atmosphere originated from old carbon, which is depleted in $\Delta^{14}C$ (refs. 128,129). Considering the current situation of global warming and ocean stratification[14], it is likely that the MCP is in a strong and increasing phase in sequestering carbon in the ocean compared to the BCP.

The MCP and the amplification of the Milankovitch theory

The Milankovitch theory is the foundation of climate evolution, which suggests that changes in the orbital parameters of the Earth can cause variations in the amount and distribution of solar radiation reaching the surface of the Earth, which can then affect its climate over long periods. The eccentricity, that is, the circularity of the orbit of the Earth around the sun, theoretically contributes less than 0.1% of the solar radiation at the surface of the Earth, yet the eccentricity cycle was the dominant cycle of climate change in the late Quaternary[130]. It is debatable how minor changes in orbital parameters could lead to incredibly large climate changes in the glacial–interglacial cycle. Recent research on deep-sea sediment records has shown that changes in solar radiation can control the terrestrial nutrient input to the ocean, which, in turn, regulates the oceanic carbon cycle. At long-eccentricity maxima (~400,000 years), summer insolation maximizes at low latitudes, along with increased regional and global seasonality. This leads to an intensified global monsoon and enhanced rainfall, increasing nutrient input to the ocean and surface productivity, which inevitably increases carbon storage in the deep ocean and decreases marine inorganic carbon $\delta^{13}C$ (the ratio of ^{13}C to ^{12}C in samples compared to the ratio in a standard)[17]. At long-eccentricity minima the opposite is true.

Such a hypothetical connection between eccentricity forcing and long-term changes in the seawater carbon isotopic signature has been simulated in a numerical model for the Miocene climate optimum over 14–17 million years. The modelling results showed that, at eccentricity maxima or minima, the intensity of continental weathering and nutrient supply lead to the minima and maxima of $\delta^{13}C$ in the ocean[131]. Therefore, the MCP could amplify the effect of the Earth's orbital forcing on climate change by regulating the deep-sea carbon reservoir (RDOCt-rich). The amplifying effect of the MCP has been manifested in climate events in the early history of Earth such as the severe glaciations in the Neoproterozoic, when the RDOCt reservoir was extremely large and could have played an even greater role in its climate than during the Quaternary[123]. This may explain why seawater $\delta^{13}C$ fluctuated with much larger amplitudes, reaching >10 per mille (‰) in the Neoproterozoic and >1 ‰ in the early Cenozoic, whilst being only ~0.3–0.5 ‰ in the Pliocene–Pleistocene[132–134]. Therefore, variations in the size of the MCP-regulated oceanic carbon reservoir on geological time scales may shed light on the eccentricity enigma of the Milankovitch climate theory.

Modelling of the MCP under climate changes

Recent advances provide a unified hierarchical model that simultaneously predicts the preservation and degradation of organic matter in geochemical systems[135]. Additionally, there is a quantitative model for the accumulation of DOM that explicitly resolves the ecological

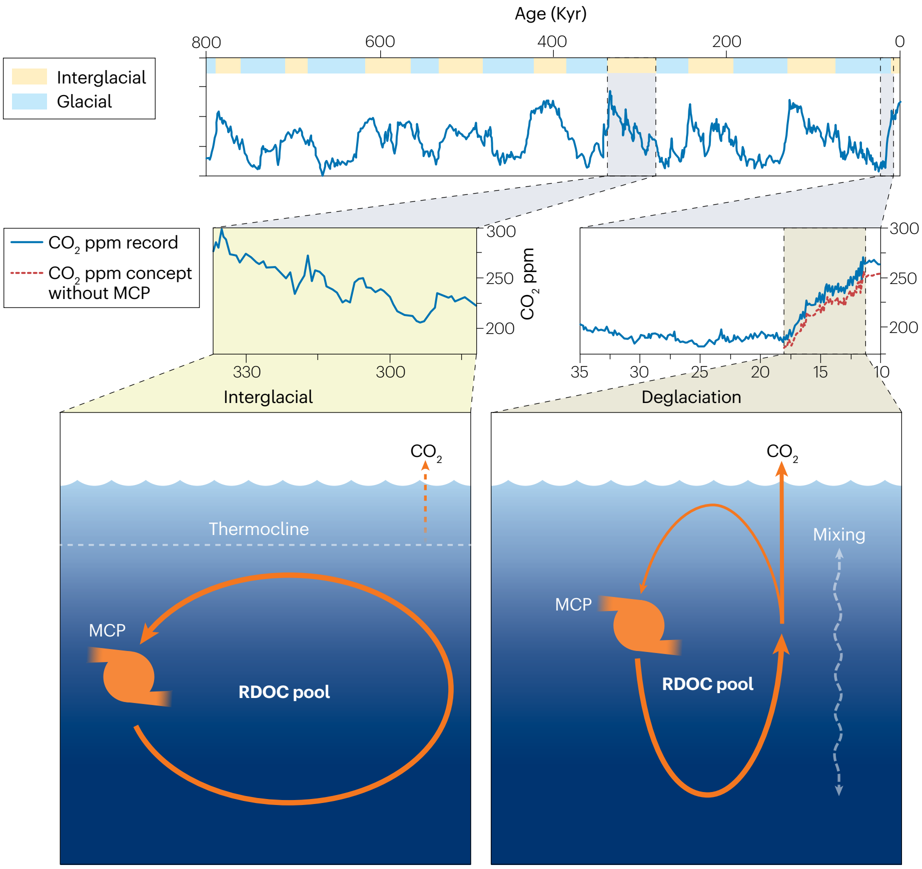

Fig. 4 | The RDOC pool driven by the MCP is a two-way regulator of climate change. During a warm period (interglacial), the deep-sea refractory dissolved organic carbon (RDOC) pool gradually builds up below the thermocline, acting as a cooling mechanism for the atmosphere (left). On the other hand, during a glaciation period, mixing of the water column remobilizes the oxidation and outgassing of intrinsically recalcitrant RDOC acting as a warming mechanism for the atmosphere (right). Both processes mitigate climate fluctuations. The trend of atmospheric CO_2 variation in the past 800,000 years has an obvious glaciation cycle process of 100,000 years. The geological history of CO_2 is known from the Antarctic ice core record (data source: Paleo Data Search). The dashed red line in the CO_2 record represents a hypothetical scenario where CO_2 release during deglaciation is delayed in the absence of the RDOC pool; values are calculated with a 0.95-fold multiplier of the original value during deglaciation to indicate a hypothetical scenario[127,152,153]. Kyr, thousand years; MCP, microbial carbon pump; ppm, parts per million.

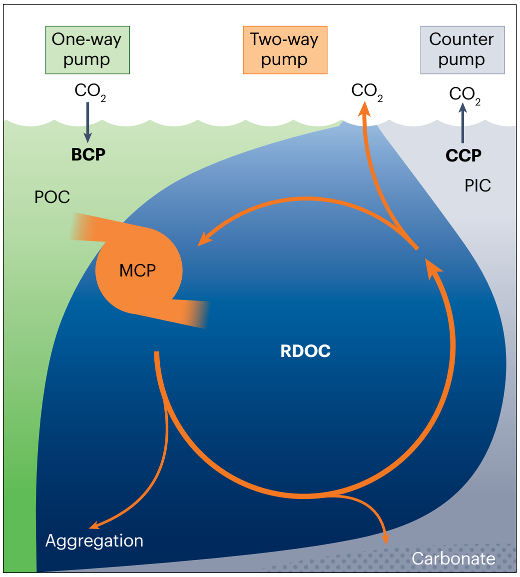

Fig. 5 | Differences between the BCP, the MCP and the CCP. The biological carbon pump (BCP) carries a fraction of the photosynthetically fixed carbon to the deep ocean to be buried in the sediment, where it is removed permanently from the ocean. Because of this, the BCP can be termed a 'one-way pump'. The microbial carbon pump (MCP) can be termed a 'two-way pump' as it stores the refractory dissolved organic carbon (RDOC) within the ocean for a long time before it is remineralized to CO_2 and is potentially available for outgassing to the atmosphere. The carbonate counter pump (CCP) is a 'counter pump' because a substantial fraction of CO_2 may be released into the atmosphere (depending on the pH of the water and the partial pressure of CO_2 in the atmosphere) when a mole of carbonate is precipitated. PIC, particulate inorganic carbon; POC, particulate organic carbon.

dynamics of consumers, which release multiple pools of DOM. The model incorporates microbial uptake by a diverse community of consumers[136]. A logical and exciting next step would be an integration of the geochemical kinetics and ecological dynamics[101].

Both ultra-high-resolution mass spectrometry and high-throughput sequencing techniques provide semi-quantitative information on the molecular composition of DOM and microbial species diversity. Advancing our knowledge of the molecular structure of DOM and microbial functional diversity provides multilayered information. The complexity of the data enables machine learning algorithms and neural networks to recognize patterns in RDOC, using the samples for training[137]. The exponentially growing application of machine learning and simulation models allows hypothesis testing. Whilst experimental approaches have moved from mainly in vivo to in situ, machine learning allows the testing of hypotheses in silico. The long-term stability of RDOC was confirmed using a neural network model that mimics the encounter probability between microorganisms and DOC in the ocean[138]. This approach utilized assumptions about uptake and degradation kinetics and simulated the age and concentrations of the oceanic DOC pool to match observations.

Synergistic effects of the carbon pumps to maximize carbon sequestration

The first step towards maximizing ocean carbon sequestration would be a comprehensive understanding of the relevant processes involved in ocean carbon storage, including the interactions between the MCP, BCP, CCP and SCP (Figs. 1 and 5). The BCP is key for ocean carbon sequestration. However, the majority of its organic carbon flux is ultimately respired to CO_2 and only a minor portion (less than 1%) reaches the seafloor for burial[5]. The production of calcium carbonate by the CCP is accompanied by the release of CO_2 into the water and atmosphere, creating a partial 'counter' effect to the uptake of CO_2. The SCP depends on the abiotic controls of the difference in $p\mathrm{CO_2}$ between the atmosphere and surface seawater and downward transport processes. The four pumps occur simultaneously, with their relative importance depending on the environmental conditions, and thus they could potentially work synergistically for carbon sequestration. For example, the MCP may enhance the BCP through collision, binding and even coating of POC with RDOC molecules[30]. The effect of the MCP on the CCP is twofold. In the water column, high-molecular-weight RDOC compounds or their aggregates could be the nuclei for carbonate precipitation[24,139]. In the sediment, the MCP promotes precipitation of authigenic carbonate; this process is driven by microbially mediated reactions that enhance alkalinity through bicarbonate and carbonate production via sulfate reduction, denitrification and anaerobic oxidation of methane[139–142]. In the surface waters, photosynthesis or application of alkaline minerals can enhance alkalinity and pH and thus uptake of CO_2 from the atmosphere[143]. Fertilization with iron[144] and aluminum[145] promotes the efficiency of the BCP and CCP and thus the transformation of DOM within the MCP. Based on the above understanding, a concept of an integrated approach of the different carbon pumps – namely, BCMS – is proposed[19]. This concept also encompasses the dual interpretation of BCMS as a 'business continuity management system' for effective risk reduction and control. The application of both BCMS interpretations (BCP–CCP–MCP–SCP and business continuity management system) would ensure that the implementation of ONCE is not only sensible and reasonable but also compliant with legal standards.

The combined carbon pumps in sea-farming fields

Aquaculture areas are prone to eutrophication, hypoxia and acidification in the bottom waters. To address these issues, artificial upwelling can be applied to bring nutrient-rich and high DIC waters from deeper levels to the surface. This promotes photosynthesis, which converts CO_2 into carbon biomass, increasing pH (>8.5) and decreasing $p\mathrm{CO_2}$ below atmospheric concentrations. This leads to CO_2 uptake (negative emission) into the ocean[38,146], thereby enhancing the carbon pumps. The accompanying down-welling can bring oxygen-rich and high-pH waters from the surface to the bottom, which mitigates hypoxia and favours CCP. We give an example in the upper Chesapeake Bay, where submerged aquatic vegetation reduces water $p\mathrm{CO_2}$ to as low as 20 ppm and increases pH to as high as 10.2, leading to substantial calcium carbonate precipitation in areas with rich aquatic vegetation. In such cases, the CCP is a positive pump, as carbonate rather than bicarbonate is dominant, and even if there is CO_2 generated from calcium carbonate precipitation, it is not released to the atmosphere but serves as a substrate for further photosynthetic production[147]. Artificial ocean alkalinity enhancements can be applied in sea-farming areas to strengthen the efficiency of the four pumps combined.

Business continuity management system in wastewater treatment plants

The current wastewater treatment protocol has a serious disadvantage in terms of carbon sequestration as it accelerates the release of CO_2 into the atmosphere by decomposing organic carbon into CO_2 (ref. 148). The discharge of treated wastewater also acidifies the receiving coastal waters[148]. Based on the BCMS principle, we propose to capture the DIC into calcium carbonate in treatment plants by using a strong base such as sodium hydroxide from electrochemical production or minerals containing magnesium hydroxide and calcium hydroxide. The remaining residual carbon will be highly refractory in both solid (slurries) and dissolved (RDOC) forms, before being released into the environment. The wastewater effluent will also serve as an effective means for ocean alkalinity enhancement via the spreading of river plumes and ocean mixing as well as mitigating ocean acidification in coastal waters[149]. It remains to be seen whether the wastewater, which is mainly composed of RDOCt, will degrade after discharge. Additionally, the ecological effects of such an increase in ocean alkalinity need to be explored[150,151].

Overall, the combined effects of BCMS are important for the design and implementation of 'best practice' carbon sequestration strategies (Fig. 6).

Conclusion

The MCP has become an active and evolving field of research, especially in its connection with RDOC compounds and microbial diversity and its role in the carbon cycle and climate change. In this Review, we have highlighted aspects where focused attention could significantly improve the understanding of MCP mechanisms and their potential applications.

In the past decade, substantial advancements have enhanced our understanding of both microbial diversity and DOM diversity. Such developments stem from metabolic and functional studies of key microbial groups, omics and bulk analyses of DOM as well as from biogeochemical models.

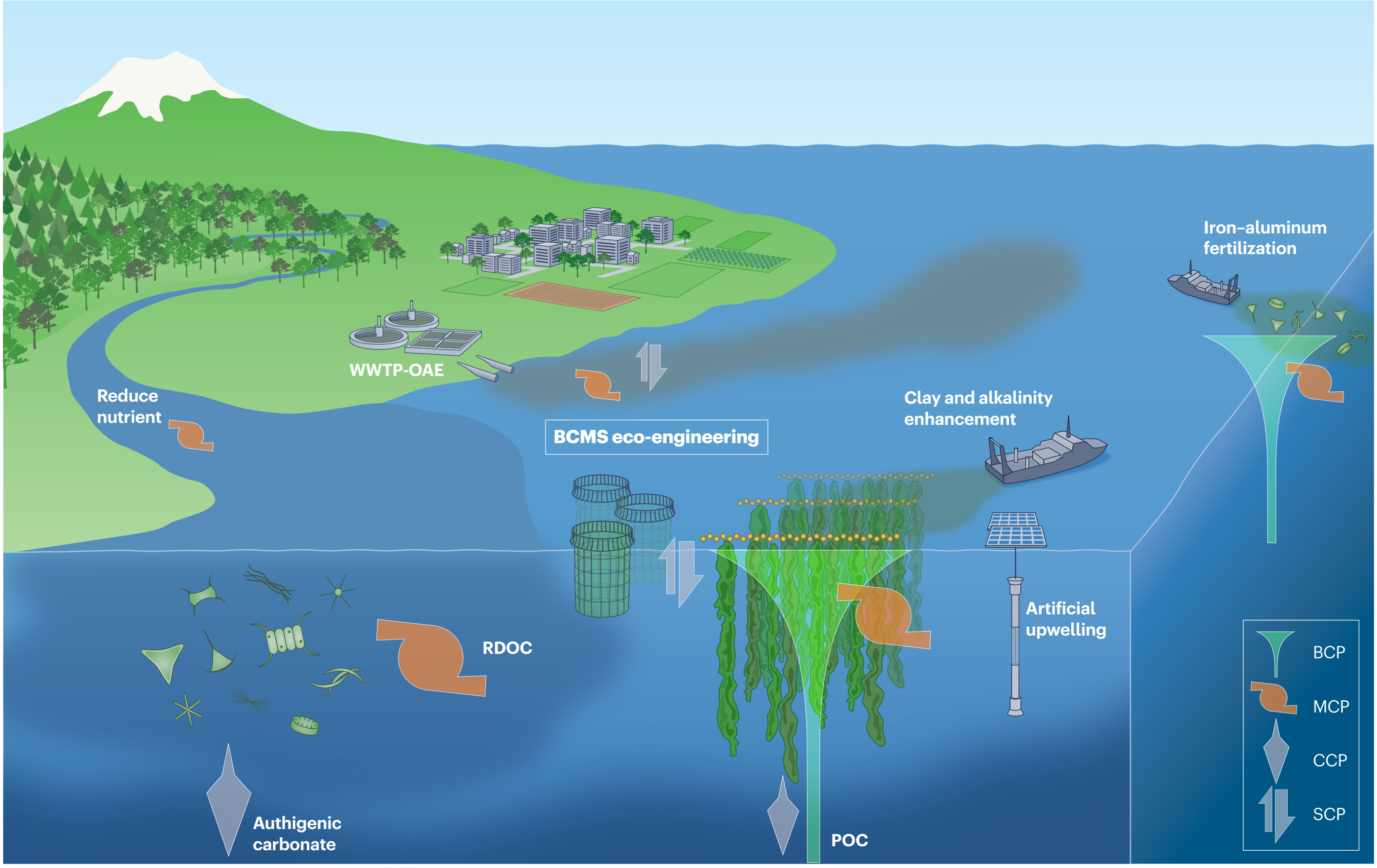

Fig. 6 | An integrated approach for maximum carbon sequestration in the ocean. A proposed integrated approach of the different carbon pumps – the biological carbon pump (BCP), the carbonate counter pump (CCP), the microbial carbon pump (MCP) and the solubility carbon pump (SCP) – named the BCMS approach, is proposed to maximize the sequestration of carbon in the ocean. Different strategies include estuarine remediation[92], whereby reduction of terrestrial nutrient inputs can enhance the overall efficiency of the four pumps by reducing respiration and water acidification, enhancing both refractory dissolved organic carbon (RDOC) and net carbon burial through biotic and abiotic processes; artificial upwelling in sea-farming fields[154,155], aimed at bolstering the production and burial output of the BCP and augmenting the MCP and sediment CCP output, while improving bottom water quality; and wastewater treatment plant (WWTP)-based ocean alkalinity enhancement (OAE)[149], which can drive the SCP in the surface ocean and increase alkalinity in nearshore areas, thereby promoting the SCP and further carbonate deposition by the CCP, whilst the dissolved organic carbon in sewage is partially converted to RDOC via the MCP[156]. Lastly, the application of iron-aluminium fertilization can mitigate iron limitation of phytoplankton growth and promote particulate organic carbon (POC) sinking, thus enhancing the efficiency of the BCP in oceanic waters. Authigenic carbonate is formed by microbial activity or chemical changes in sediments (see the section 'Synergistic effects of the carbon pumps to maximize carbon sequestration'). Adapted with permission from ref. 149, Elsevier.

With the accumulation of big data, more data science and systematic science approaches should be applied in future studies of complex interactions between microorganisms and DOM. Multilayer networks will help to elucidate the functional relationships between microbial species and DOM molecules to further illustrate the formation of RDOC from microbial activities. These models, together with in silico simulations of long-term climate change impacts, can showcase the mechanisms behind microbial RDOC production and the efficiency of the MCP.

Faced with increasingly severe climate change issues, numerical simulations of past and present marine microbial processes will not only help to understand the potential response of the MCP to climate change but also provide possible avenues for research on ocean carbon sequestration. Further insights into the microbial and biogeochemical processes associated with the MCP, their interactions with the other carbon pumps, and their potential applications for carbon sequestration would be maximized through the production of a virtual 'digital twin' replicating real-world scenarios. Additionally, machine learning and numerical models can generate geological event-based scenarios. The outcome of these approaches would also help the evaluation of ONCE or marine CO_2 removal techniques and future projections of ocean carbon storage.

Microbially driven RDOC has acted as a buffer against climate change throughout the history of Earth. Studies over the past decade have provided a wealth of data on both microbial biomolecular and ecological processes as well as on RDOC compounds and their recalcitrance. However, critical gaps persist in understanding the link between different mechanisms, their interactions and their biotic and abiotic controls. To address these gaps, real-world observations, experimental and modelling studies, and digital twin simulations are needed. It is particularly desirable to understand the processes and their environmental boundary conditions to promote the synergistic effects of the four ocean carbon pumps (BCMS) for efficient carbon sequestration. Linking microbial taxonomic and functional diversity, not only with the chemical diversity of DOM but also with the processes and synergistic interactions within the BCMS, offers a systematic approach to understanding microbial-driven carbon cycling and carbon sequestration.

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