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A Study on the Bio-Limiting Nutrient Circulation in the Ocean's Oxygen Minimum Zone

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Abstract

The ocean's Oxygen Minimum Zone (OMZ) is known to be biogeochemical complex in terms of nutrient mass-balance and major element cycles. The recent reports suggesting that the ocean's OMZ facilitate about 25%-50%loss of nitrogen in the ocean predominantly by anammox coupled with the recent identification of the major contribution of DNRA to oceans NH_4^+ flux, further complicates our understanding of the oceans nitrogen circulation and budget. Also, studies have shown that OMZ promotes the occurrence of sulfidic plumes. Moreover, the redox sensitivity of the ocean's OMZ such as their active sulfate reduction and sulfide oxidation potential makes them important regions for the cycling of phosphorus. However, as have been predicted that future expansion and intensification of OMZ driven by climatic change, still the understanding of this biological system remains a challenge with regards to its role in the overall chemical budget of the ocean.

In this regard, we aim to provide a comprehensive summary of the overall circulation patterns of some essential but biologically limiting nutrients such as nitrogen, sulfur and phosphorus in this OMZ of the ocean. This will benefit future researches on predicting global budgets of these nutrients and their cycles related to the marine environment as it will help bring out a good understanding of the inextricable link among each of these limiting nutrients, as have been researched and reported in varied ways.

Keywords: Bio-limiting nutrient; Nitrogen; Phosphorus; Sulfur; Oceans oxygen minimum zone

Introduction

Dissolved Oxygen Concentration (DOC) is one of the most important indexes for the thriving of marine ecosystems and a key factor in determining the energy direction in the marine trophic levels. DOC is equally the powerhouse for biogeochemical cycles, ocean nutrient circulation, biological production near the surface and the degradation of organic matter in the oceans interior [1-5]. However, certain layers especially the mid-layers of the present-day ocean is characterized by a low level of dissolved oxygen. DOC decline in the mid-layer of the water column arises when organic matter oxidization exceeds its availability in less ventilated zones, thus from a hypoxic layer commonly referred to as the Oxygen Minimum Zone (OMZ) [6-12]. This immerse recognition of the OMZ is as a result of its revealed expansion, intensity, and its role as a key to understanding the present unbalanced and altered nitrogen, carbon iron, phosphate cycle. The increase in hypoxic layers of the ocean is a direct consequence of global warming that causes the decline in oxygen solubility, concentration, and its vertical exchange in the ocean, thereby slowing down the oceans interior ventilation through propagated stratification [13,14]. As nitrate is depleted or used up, sulfate dominated reducing microbes assume, controlling the biogeochemical process involved in the cycling of marine sulfur. Also, hypoxia facilitates the greater recycling of Phosphorous (P), from sediments [15-20].

Literature Review

The oxygen minimum zone of the ocean occurring in mid-layer of the water column is hostile and inhabitable to metazoan life but is characterized by declined high trophic level diversity but abundant pelagic microfauna [21]. The microbial community in the OMZs possess assemblages of diverse genetic repertoire of putative sulfate, nitrate, and phosphate reducing bacteria whose combined metabolism plays intimate roles in its biogeochemical cycles and therefore which permits and enhances the use of alternative electron donors and acceptors during energy metabolism [22-30]. Specifically, OMZs are harbored by bacteria and archaea that arbitrate and facilitate the loss of oceanic fixed nitrogen to the atmosphere through denitrification and the recently discovered anaerobic oxidation of ammonia to N_2 [31,32].

This review presents an overview of the cycling of some basic vital marine elements (nutrients) and how the overall declines in ocean oxygen concentrations affect their circulation, balance and availability in the ocean based on published reports [33]. It's hoped that the summarized information in this article would help improve our understanding of OMZ involvement in the circulation of these nutrients. This may facilitate a realistic assessment of the short and long term impacts of ocean de-oxygenation on the cycling of these

nutrients in the ocean's OMZs, as well as predict the future budgets of these nutrients in the ocean [34-40].

Bio-limiting nutrient circulation in the ocean's OMZ

The availability of bio-limiting nutrients such as nitrogen, phosphorus and sulfur other than H_2O and carbon, are necessary supporting nutrients required for primary and biological production [41]. Biological limiting nutrients can be absorbed by primary producers *via* roots from the soil and in aquatic systems directly from solution/water to boast primary production. However, the availabilty of these essential nutrients in the ocean is threatened by the decline in DOC which has been observed to be facilitated by temperature increase [42-47]. In addition, observations from four modeled based assessment, it was shown that global warming caused declines in marine productivity at lower altitudes, suggesting that the recycling of these nutrients in marine environments is undoubtedly affected by stratification of the water column [43-55]. Nitrogen limitation affected primary production in Eastern Tropical North Atlantic (ETNA) and Eastern Tropical South Pacific (ETSP). Despite the numerous reports on the effects of global warming on nutrient circulation and marine productivity, there is still low confidence and insufficient measurement of the present and predictions of the future net primary productivity of the oceans [56,57]. Also, there is no clear distinction of climate induced signals on primary production and that of those resulting from natural variability as have been explained earlier [58-65].

Nitrogen circulation in the ocean's OMZ

Nitrogen plays a major role in the biogeochemistry of the marine environment with considerable influence on the cycling of other elements, particularly carbon and sulfur. However, the fluxes of nitrogen in the ocean is affected by the balance between ambient oxygen concentration which is determined by the O_2 supply and remineralization of sinking Particulate Organic Carbon (POC) [66,67]. In oxygen sufficient regions of the ocean, nitrification, a biologically enhanced process converts NH_4^+ to NO_2^- and NO_3^-, whereas in anoxic ocean regions, nitrate, is generally known to be reduced in a stepwise manner to N_2O or N_2 ($2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2$) for the respiratory oxidation of organic matter [68-70]. Though, emphasized to be a hostile environment for almost all marine life, and cover about only about 7% of the oceans, global estimates show that the oceans Oxygen Minimum Zones (OMZs), promote about 25%-50% of the removal through anaerobic microbial activities especially anammox denitrification, of oceanic fixed nitrogen. Thus, OMZs are known to be the focal zones of oceanic nitrogen loss through denitrification and may cause lower nitrate concentrations in upwelled water [71-75]. Studies of the past geological records of sediments provides evidence of the important roles OMZ and coastal-offshore OMZ-water mass exchange play on the overall N budget. The role OMZs play in the nitrogen circulation especially its loss through heterotrophic and anammox denitrification has been evinced through several *in-situ* experiments. The diversified decadal measurement of the rate of nitrogen loss in the OMZ of oceans, employing methods, such as direct quantification of nitrogen gas, its ratios with Argon (N_2:Ar), stoichiometric approaches and electron transport activity assays etc [76,77]. for areas such as those of the ETSP, ETNP and the Arabian sea are employed. However, none of these methods has been able to distinguish N_2 production resulting from anammox denitrification and that of heterotrophic denitrification. Also the rate and regulatory

pattern involved in the production and release of N_2 by each of these processes yet to be established [78-84].

Anammox denitrification is also known as bacterial oxidation of ammonium with nitrite under anoxic conditions (anammox) to produce N_2 ($NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$). During N-cycling processes, the substrates required for anammox denitrification, NH_4^+ and NO_2^- can be obtained from reduction of NO_2 through heterotrophic denitrification processes and other possible sources such as nitrification (nitrate reduction to nitrite or the oxidation of NH_3) and the oxidation of organic matter through Dissimilatory Nitrate Reduction to Ammonium (DNRA), (NO_3^-/NO_2^- to NH_4^+) and possibly excretion by zooplankton though remains to be established. Observations from the Peruvian and the Arabian Sea OMZs shows that NO_3^- reduction significantly correlated with depth-integrated NO_2^- concentrations which suggests that that NO_3^- reduction is a major contributor to the secondary NO_2^-. Similarly, an annual estimation of about 51% and 65% of NO_2^- oxidation from coastal and offshore OMZ, respectively, of NO_3^- reduction of the ETSP was discovered. This observed occurrences, in the OMZs, suggests active N-loss in the ocean [85-92].

With the DNRA pathway, the anammox bacteria through multi haemnitrite reductase convert nitrates into nitrites and eventually to ammonium which is then combined with nitrite to form nitrogen gas. In early studies of the relative contributions of these process to marine nitrogen losses estimated through sealed sediments/water amended with 15N-labelled nitrogen species, DNRA was assumed to be insignificant compared with heterotrophic and anammox denitrification as anammox bacteria can also produce 15N15N from 15N nitrate, even in the absence of dissimilatory nitrate reducers [93,94]. The combined reactions of these reactants with anammox could be derived from the recovery of the label in the produced N_2 and may result in the production of a double 15N labeled N_2 (15N15N), which in recent studies is tagged to complicating the analysis of the data during isotope-pairing experiments. However, identified in the anoxic Peruvian shelf and upper slope sediments that, DNRA contributed up to 80% to the total benthic NH_4^+ release as the major proportion of the total $NO_3^- + NO_2^-$ uptake was routed into DNRA [95-98]. Likewise, DNRA at the shallowest station of the Peruvian contributed up about 63% (12.4 mmol m^{-2} d^{-1}) to the total NH_4^+ flux. In OMZ off the coasts of Peru and Namibia, DNRA has been found to occur in regions where denitrification was not detectable but low rates of DNRA was detected, but also undetected in ETSP. However, the potential of DNRA to occur in open waters is still insufficiently explored and the distinction between the supply of NH_4^+ and NO_2^- from DNRA and the other mentioned sources have not been extensively explored [99,100].

Aside the contributions of DNRA, nitrification etc. processes to the thrive of anammox denitrification in oceans OMZ, *ex-situ* sulfide incubation experiments within the Chilean OMZs suggest that cryptic sulfur cycling contributes about 30% of the of carbon mineralization and the subsequent release of NH_4^+ for anammox. There has also been a recent discovery of as a potential niche for NO_2^- dependent n-damo, a methanotrophic and sulfate-dependent bacteria responsible for anaerobic oxidation of methane whose pathway reduces NO_2^- to Nitric Oxide (NO), which is then putatively dismutated into N_2. These imaging scenarios coupled with the predicted future expansions and intensification of the oceans OMZs, suggest that the future global losses of nitrogen may increase [101]. However, a confirmation of the potential for the activities of the n-damo in the pelagic OMZ and the

inclusion of these nitrogen loss contributing factors/activities in assessment of global nitrogen budgets is still lacking. Also, despite the significant effects nitrogen losses imprints in seawater nutrient, especially ratios of nitrogen to phosphorus and reduces the availability of nitrates for primary producers such as phytoplankton. However, these studies are still speculative, as biogeochemical models do not reproduce present-day global patterns of N [102,103]. Also, with the existence of OMZ in the oceans and its predicted vertical expansions in the near future in response to global warming we suggest the possibility of a growing and thriving mass of the denitrifying anammox bacteria, therefore we recommend further studies in other to determine the relative global distribution of this bacteria which is seldom studied [104-110].

Sulfur circulations in the ocean's OMZ

Regions of the oceans that are characterized by extreme hypoxia or worse cases of anoxia such as the OMZ of the ocean, facilitates the degradation of organic carbon leading to the production of Hydrogen Sulfide (H_2S), from the heterotrophic mineralization of organic matter by giant Sulfate (SO_4^{2-}) reducing bacteria. Under well balanced circumstances, such as a steady state where the diffusive fluxes of nitrate and sulfide are in a 1:2.5 ratio with sufficient concentrations O_2, sulfide-oxidizing and nitrate-reducing these bacteria are capable of detoxifying sulfide into sulfur, preventing its release into the water column and reducing the frequent occurrence of sulfidic events [111]. On the other hand, in the oceans oxygen minimum zones, observed sulfide, a product of reduced sulfate often originates from sediments of nitrate and nitrite depleted waters that act as terminal electron acceptors for the oxidation of H_2S as the reduction of NO_3^- and $NO2-$ to NH_{4+} is accompanied by oxidation of dissolved Sulfide (H_2S) to a Sulfate (SO_4^{2-}) *via* elemental sulfur as a reactive intermediate [112]. Under these nitrate and oxygen deficient conditions, the accumulated concentration of sulfide reaches higher concentrations as it diffuses into the pelagic water column. In time series station in the Baltic Sea, a possible occurrence of frequent sulfidic plumes events which is likely to also occur in other eutrophication and OMZs hot zones such as the Atlantic and Pacific oceans. The massive *Beggiatoa* and *Thioploca* microbial communities harbored by the OMZ of the ocean e.g. OMZ sediments of the Arabian Sea, the Benguela current ecosystem off Namibia and that of the Basaltic sea etc. significantly reduce the sulfide flux from the sediments to the overlying water column. The quantified release of this toxic substance (H_2S) especially from the underlying sediments into the water column can lead to the occasional build-up of high concentrations of H_2S in bottom water e.g. diatomaceous sediments of Benguela current upwelling system and the SO_4^{2-} reduction by pelagic microorganisms within the water column enhances its buildup in oceanic waters e.g. Black sea, promoting the loss in marine life and deterioration of the marine ecosystem at large [113]. Also under overextended conditions of declined bottom water Oxygen (O_2), NO_3^- and NO_2^-, microbial sulfide production can overcome the sulfide oxidation capacity of the sulfur bacteria and lead to marine sulfide poisoning of life. In an attempt to determine the nitrate and nitrite concentration in the Peruvian OMZ discovered that, sediments had a high potential for sulfide release and began to release sulfide as soon as NO_3^- and NO_2^- become depleted. Furthermore the results from pore water geochemical and non-steady state model techniques employed by to determine how sediments with nitrate-storing bacterial communities respond to NO_3^- and NO_2^- depletion, predicted an almost immediate increase in sulfide fluxes when NO_3^- and NO_2^- where exhausted [114-118].

The metabolism of sulphur is considered primitive and genes related to its oxidation and reduction are dispersed throughout the bacterial and archaeal domains. Sulfur-oxidizing bacteria may be linked to that of the dissimilatory metabolism of oxidized nitrogen species as genomic analysis of the lineage SUP05, a free-living *gammaproteobacteria* relative of clam endosymbionts from the a North Pacific seasonal OMZ, revealed enzymes necessary for the chemolithotrophic oxidation of reduced sulfur, as well as those for nitrate reduction to nitrous oxide (N_2O). Furthermore, the discovery of the bacteria, *Epsilonproteo* in the deep sea are thought of as being involved in the cycling of marine sulfur [119]. Advanced studies done, has shown that the bacteria Gamma may also be involved in the oxidizing of sulfur in the hypoxic marine water columns and both bacteria have an overlapping but slightly different distribution, potentially related to different redox potentials. *Gammaproteobacteria* were identified in the free nitrate-rich OMZ waters off the Chilean coast suggesting its involvement in the cycling of sulfur. Likewise, in sulfide-free but nitrate-rich regions of the Saanich Inlet, sulfide-oxidizing and nitrate-reducing genes were found. Past studies have shown that the sulfur producing species have been reduced as they are predated and oxidized by heterotrophic, chemolithoautotrophic bacteria, reducing their threat to releasing hydrogen sulfide. However, a series of shipboard incubation experiments from current studies of waters obtained from OMZs demonstrates active sulfate reduction and sulfide oxidation. OMZ waters promotes pronounced sulfate reduction and likely responsible for substantial NH_4^+ production. However, concise evidence connecting sulfate reduction and NH_4^+ production is still insufficiently explored [120].

Also oxygen, nitrate, nitrite, nitric oxide, and nitrous oxide utilizing and distinct chemolithoautotrophs, γ-, δ- and ε-proteobacterial taxa involved in the oxidation or reduction of sulfate in what they expressed as the largest plume ever recorded in oceanic waters, that occurred at the OMZ off Peru. This could be a consequence of the climate change accelerating temperatures and ocean stratification and subsequently facilitating the (H_2S) production rate, however direct field observations are lacking. Likewise, the activities of the *Thioglobus perditus* together with free-living SUPO5 bacteria in the Peru upwelling and their dispersal facilitated by mesoscale eddy-driven cross-shelf, was identified. However, the cell abundances, distribution, metabolic activities/capabilities of this free-living SUPO5 bacteria in the global ocean is still insufficiently explored [121].

The sulfur cycle has been proposed as a partial solution to the biogeochemical problem of closing marine fixed-nitrogen budgets in OMZs. However, the recent discovery of the cryptic sulfur cycling which refers to the simultaneous activity of sulfate-reducing and sulfide-oxidizing pathways in a closely defined space such as a marine particle aggregate, has been attributed to be contributing to the loss of fixed N from productive upwelling regions, the production of climate-relevant N_2O and dark carbon fixation in the sub-euphotic water column. These reductions of the sulfate is said to only be active in the presence of thermodynamically fully utilized electron acceptors such as nitrate and nitrite, but some challenged this idea in their recent experiments suggesting that an active, but cryptic sulfur cycle is present in non-sulfidic subsurface waters in the eastern tropical South Pacific OMZ off northern Chile and concluded from outcome of their calculations, that sulfate reduction is still a thermodynamically favorable process in these OMZ waters. However, more studies on this should be done to rule out these speculations. Also, speculations of other OMZs of the global oceans, to be reservoirs of actively coupled sulfur and nitrogen cycles most especially the cryptic sulfur cycle

must be addressed for accurate global assessment of the balance of this nutrient in the ocean.

Phosphorus circulation in the ocean's OMZ

Phosphogenesis is responsible for the removal of terrestrial phosphorus in the form of phosphate by intense weathering of sedimentary basins accumulated with phosphorous. Phosphate is one of the biogeochemical limiting nutrients whose existing percentage determines how much carbon is incorporated into the living biomass and how much is consumed during the growth of phytoplankton in the aquatic environment.

In the marine environment, phosphorus rapidly undergoes recycling in the water column but some organic components of it, stretches to the sediments especially under hypoxic conditions such as OMZ, as particulate organic matter such as phytodetritus, including those absorbed by iron oxyhydroxides and are later degraded at a certain depth, releasing HPO_4^2, limiting their sedimentary deposition. The sedimentary phases of Phosphorus (P) include but not limited to exchangeable P, Ferric Fe associated P, authigenic, biogenic and $CaCO_3^-$ bound P, detrital P and organic P [122].

Under extended burial conditions, the labile P converted to $HPO4^2-$ and released from the sediments undergoes diffusions or precipitation as authigenic calcium phosphate minerals such as $Ca5(PO_4)_{3-x}(CO_3)_x(OH,F)$. These chemical forms of P in deposited sediments are a reflection of the redox and can be used to reconstruct the depositional conditions from sedimentary records. However, the burial efficiency of P is altered by the concentration of benthic oxygen, as it influences the reduction of the iron oxyhydroxides in reducing surface sediments, which decreases the capacity of the sediment to retain upward diffusing dissolved phosphate. It also alters the release of P from organic matter enhanced relative to carbon under reducing conditions.

Phosphates can be deposited as sedimentary rocks, formed from a series of biological actions coupled with mineral precipitations. Oceanic anoxic events play a major responsibility in the substantial deposition of phosphorite from the geological past, usually from preferentially regenerated from P-bearing organic matter as compared to carbon, such as black shale. Much of the regeneration takes place in the water column but in sediments of relatively shallow water bodies.

The decline in oceanic oxygen has a marked effect on the cycling of phosphorus as under hypoxic conditions, phosphate (TPO_4) is dissolved and released into the pore fluids and subsequently into the overlying bottom water. Iron oxyhydroxides absorb this released phosphate and reduce them through microbial induced dissolution and the associated liberation of metal-oxide-bound phosphate, into absorbable states (soluble states), all enhanced under oxygen-deficient conditions. Hydrogen sulfide may then further enhance the phosphate released from the oxyhydroxides through reductive dissolution. Studies on the mechanisms of phosphorus cycling especially in the hypoxic region of the ocean are still insufficient, therefore, more laboratory, field, predictive future phosphorus flux models and assessment of the distribution of phosphorus using eg. remote sensing etc. shloud be done to build a comprehensive understanding of this component of our environment. Phosphogenesis is likely driven by large sulfur bacteria from the filamentous, highly motile genera *Beggiatoa, Thioploca* and non-motile *Thiomargarita* because of their marked frequent and large existence as fossils in phosphorite rocks in active regions of modern phosphorite formations. Likewise, the occurrence of phosphorus is also linked to the result of oversaturation in the pore water with respect to apatite induced by the activity of microorganisms such as large sulfur bacteria, *Thiomargarita*, and the phylogenetically and metabolically closely related genus *Beggiatoa*, that results in its precipitation.

Discussion

Dating back to 1986, the release of phosphorus upon the addition of sulfide which acted as a stimulant. In additions, they found out from their quest to ascertain whether "acetate or sulfide is responsible for the release of phosphate by a marine *Beggiatoa* strain through the decomposition of polyphosphates" that, phosphorite is formed preferentially in sediments with high sulfate reduction rates. Despite the discovery of the different sources and formation processes of phosphorite, a clear distinction of biologically available phosphorus and that of dissolved organic phosphorus from lateral fluxes and their significant potential transformation mechanisms, is still under discovered in hypoxic waters of the global ocean.

Regions of local upwelling, where sulfate reduction rates are exceptionally high are characterized by pronounced phosphogenesis as they are formed in shelf sediments that are located at the border of oxygen-depleted water masses. In occasions where bottom waters are oxygenated and nitrified, polyphosphate commonly referred to as poly-P and nitrates accumulated and stored in vacuoles *Thiomargarita namibiensis*, are speculated to be taken up during short periods. Consequently, when oxygen concentration drops to zero (anoxic), energy from the hydrolysis of the polyphosphate is gained by the *Thiomargarita namibiensis*. Anoxic bottom-water conditions coupled with regions where sedimentary iron cycling plays a major role in organic matter mineralization and also promotes the benthic regeneration and reflux of inorganic phosphate to the water column. Active phosphogenesis is mainly found beneath the nutrient-rich upwelling areas off the coasts of Peru, Chile and Namibia, in modern oceans, representing the major hotspots. However, during studies of microbial marine phosphorus cycle, the direct measurement of microbial phosphorus is difficult to achieve as for example, DNA sequences need to be measured directly or removed or its influence terminated during the DNA sequence analyses of diagnostic P-cycle but this practices is lacking. Also, the global assessment of the gains and the losses of phosphorus together with their distinctive loss pathways are still rarely if there is any, explored in the marine oxygen-starved regions.

Conclusion

Climate-induced ocean oxygen declines and the predicted future further declines threaten the balanced distribution of the ocean biodiversity as it controls and alters the cycling patterns of basic biologically limiting nutrients such as sulfur, phosphorus, and nitrogen. The sensitivity of N loss processes in response to minimal changes in O_2 potential for additional processes, such as preferential of sulfide and phosphate released directly in the water column drives the oceanic nutrient balance. The excess or limited production of these nutrients has a marked effect on the survival of the inhabitants of the marine environment and OMZ plays a major role in this.

However, global estimations of how much and at what rate sulfide is generated in the water column during a sulfidic event are not well resolved. Further investigation should be made to determine the distribution of these nutrient cycle altering organisms with depth and their specific niches. Also, the discovered combined effect of the eddy-driven cross-shelf transport and of *T. perditus* to denitrify and

thrive on elemental sulfur in the absence of dissolved sulfide should be further investigated. Much attention should also be given to the uprising cryptic sulfur cycle, to ascertain if there are any associations with the cycling of the other limiting nutrients such as carbon, phosphorus, etc. since it is linked with nitrogen cycling that in turn, has the influence of other biochemical cycles. Furthermore, global assessment of the gains and the losses of phosphorus together with their distinctive loss pathways are still rarely if there is any, explored in the marine oxygen-starved regions (OMZ).

Acknowledgments

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