

Preface

Biogeochemical Cycling in the Low Oxygen Marine Environments

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Biogeochemistry is the interdisciplinary science of the composition and cycling of chemical elements. Nitrogen and oxygen are two elements that are essential for living organisms and the sustenance of life on Earth. While oxygen is needed for respiration, nitrogen is required for the genetic material, proteins, peptides and enzymes in all living organisms. Oxygen minimum zones (OMZs) are regions in the world's oceans where the dissolved oxygen (DO) concentration in the sub-surface waters falls below the normal levels ($<90 \mu\text{M}$; hypoxic). These regions are situated in the eastern tropical north and south Pacific, eastern tropical north and south Atlantic and the northern Indian Ocean. When the DO concentrations fall below $5 \mu\text{M}$ (suboxic), the facultative bacteria switch to utilizing nitrate as a terminal electron acceptor in their respiration. This results in the loss of nitrogen through denitrification and anammox processes in the OMZs (please see marine nitrogen cycling in Fig. 1; Naqvi, 1991; Ward et al., 2009; Lam et al., 2011). Where the oxygen concentration is low, a suite of organisms (from microbes to mammals) can adapt and survive in these extreme conditions. In addition to these specialised pelagic regions, $\sim 0.3\%$ of the seafloor is permanently exposed to low oxygen conditions (Helly and Levin, 2004). In these regions, benthic organisms are adapted to low oxygen conditions and are involved in carbon preservation.

Low oxygen environments, such as OMZs, also generate green-house gases such as nitrous oxide and methane. Recent reports suggest the intensification and expansion of existing OMZs and the formation of new dead zones, devoid of aerobic organisms, in the coastal seas (Diaz and Rosenberg, 2008; Stramma et al., 2008; Brietberg et al., 2018). These may have socio-economic implications. Algal bloom formation resulting from massive input of nutrients from land (sewage and agriculture) may result in excessive consumption of DO, thereby impacting fish life and inturn commercial and recreational fisheries. The hydrosphere and biosphere hold only a fraction ($< 0.015\%$) of the earth's

nitrogen, and while excess nitrogen can lead to loss of DO, the availability of fixed nitrogen can limit productivity. Up to 40% of the fixed N loss from the ocean occurs in the world's OMZs (Devol, 2008). Understanding the fate of low oxygen environments and its impact on its ecosystems is clearly of utmost importance under the climate change scenario. This, in turn, highlights the need for intense research activities and understanding of such systems. This special issue entitled "Biogeochemical cycling in the low oxygen marine environments" is published to recognise the achievements of Dr. S.W.A. Naqvi, an eminent oceanographer from India, who spent his lifetime studying low oxygen environments (both marine and terrestrial) and has contributed immensely to the understanding of these systems. The issue opens with a brief bio-sketch of Dr. Naqvi and is followed by 12 articles about low oxygen environments spanning the coast, continental shelf and the open ocean. The highlights of these articles are given below.

While the OMZ in the open Arabian Sea (AS) experiences nitrate reduction, the seasonal low oxygen condition off the west coast of India is more extreme and the waters there show sulphate reduction (Naqvi et al., 2000). Bardhan and Naqvi provide the first data on the dual isotopic composition of nitrate from the World's largest coastal seasonal low-oxygen zone. They find denitrification as the major nitrogen loss pathway in the anoxic waters, however, with the co-occurrence of nitrite oxidation. The west coast of India also produces very high concentrations of nitrous oxide (up to 800 nM) and dimethylsulphide (DMS, up to 500 nM) during the seasonal low oxygen conditions. In a time series study, Bepari et al. showed high seasonal and inter-annual variability of DMS and dimethylsulphoniopropionate (DMSP) in the waters off the west coast of India during periods when the phytoplankton community was changing. Extremely high DMS concentrations (up to 440 nM) were observed in the bottom waters in the absence of DMSP, the precursor of DMS, during the seasonal anoxia suggesting a benthic source for DMS. The low oxygen conditions also impact the phytoplankton. Gauns et al. showed that the onset of oxygen-deficient conditions along the western continental shelf of India greatly altered the phytoplankton community structure, with pico-autotrophs and pennate diatoms found dominating the autotrophic biomass in oxygen depleted waters. In the same waters, a study on the culturable bacteria by Gomes et al. revealed that close to 77% of the cultures were nitrate reducers.

In contrast, the OMZ of the open ocean AS is perennial. Shenoy et al. showed significant seasonal and inter-annual variations in the OMZ. They demonstrated for the first time how the Indian Central Waters supply oxygen to the OMZ, impacting the ambient DO and nitrite distribution. They also postulate how Rossby waves influence the supply of oxygen to the OMZ and thus play an important role in the OMZ biogeochemistry. While ship observations are sparse and expensive, some recent

technical advances have opened new avenues for studying low oxygen systems. Wojtasiewicz et al. used biogeochemical and bio-optical sensors data from the BIOARGO floats (ARGO floats with biogeochemical sensors) to demonstrate the potential of these sensors to study biomass distribution under low oxygen conditions in the AS.

Though the AS and the Bay of Bengal (BoB) occupy similar latitudes, the AS experiences denitrification, which is thought to be absent in the BoB. Thus, understanding the microbial population from both these basins is of utmost importance. Menezes et al. used modified agar-based media to study the diversity of culturable sulphur-oxidising bacteria in both the AS and BoB, and observed *Proteobacteria* as the dominant phylum. Apart from the water column, Kurian et al. studied the factors controlling the organic matter distribution in OMZ sediments from the continental slope off western India. They found that the bottom water DO play a minimal role in the organic matter (OM) preservation compared to productivity in these sediments. Also, sedimentation rates, winnowing and type of OM controlled the organic-richness in the late Holocene sediments.

Although the Indian Ocean is considered as a key region for N₂O production and emission, most studies have focused on the northern part of the basin. The results of extensive N₂O measurements and first reported open ocean measurements of hydroxylamine (NH₂OH) by Ma et al. in the southwest Indian Ocean (SWIO) demonstrated enhanced N₂O saturations between 5-10°S as a result of wind-driven upwelling. This area acted as a weak source for the atmospheric N₂O inventory with nitrification as the major N₂O formation pathway in the SWIO.

The eastern boundary upwelling system of coastal Peru and Chile supports high primary production, contributing to an OMZ in the subsurface waters with high OM deposition rates in the underlying sediments. Farias et al. used ten years of time series data to aptly demonstrate the utilization of DO and formation/consumption of nitrogen species on an annual scale. Their consumption of DO was observed to be higher than the net DO transport in the aphotic zone. Different microbial activities reflected the dynamics of DO and N-species as suboxic/anoxic conditions promoting strong NH₄⁺ and NO₂⁻ accumulation in the aphotic zone. Studies on anaerobic ammonium oxidation (anammox) and denitrification in the Peru margin sediments by Rich et al. reported an advanced understanding of the role of anammox in the sediments and the potential controls on anammox rates. Results suggested that anammox contributed significantly to the N₂ production in Peru margin sediments, except in shelf sediments with high decomposition rates and dense *Thioploca* mats.

The final manuscript deals with the release of Fe-binding ligands during the LOHAFEX experiment, which was conducted in a cyclonic eddy located in the Atlantic sector of the Southern Ocean.

Laglera et al. presented the evolution of the organic speciation of iron in the upper 200 m of the water column during the experiment by a competing ligand equilibrium method using voltammetry. The paper describes Fe-cycling in detail with various sources and sinks of Fe-binding ligands, highlighting the role of copepod grazing for ligand build up and changes in organic speciation of iron.

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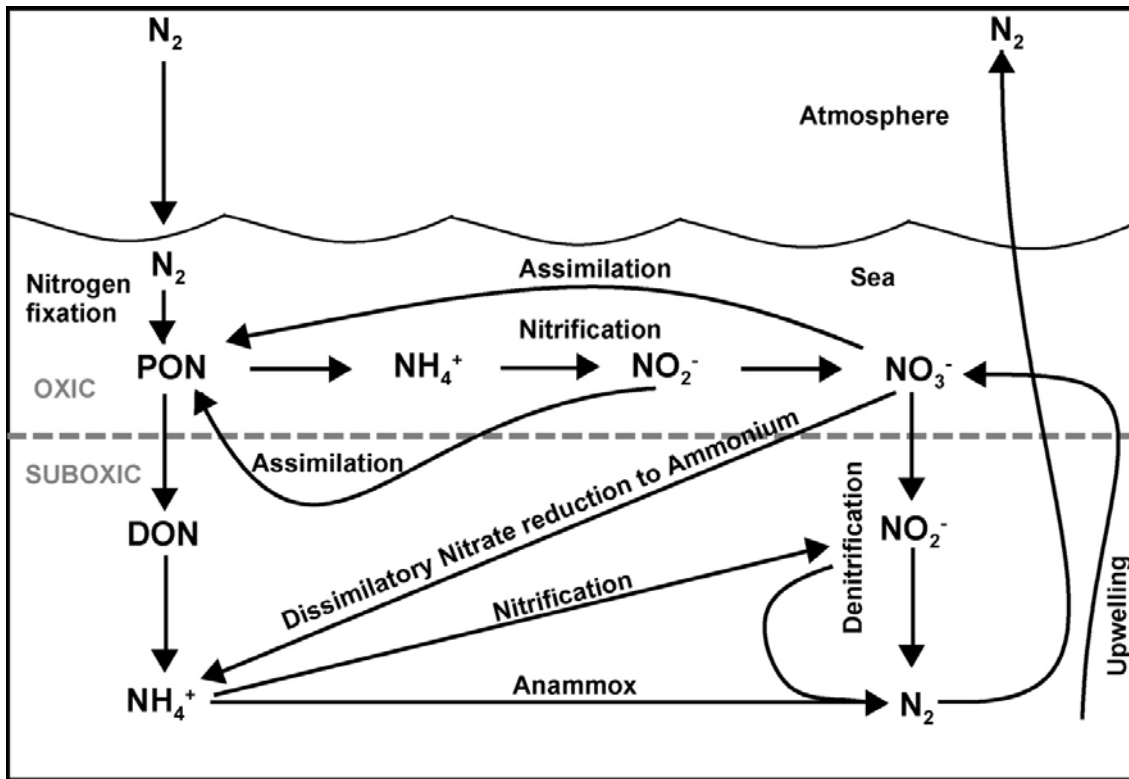


Fig.1. The marine nitrogen cycle showing the various transformations of nitrogen in the sea and the interaction between the sea and the atmosphere.