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# The Pharma Innovation



ISSN (E): 2277- 7695 ISSN (P): 2349-8242 NAAS Rating: 5.23 TPI 2021; 10(7): 972-976 © 2021 TPI www.thepharmajournal.com Received: 01-04-2021 Accepted: 06-05-2021

Puja Singh

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal, India

Shiva Kumar Udayana

M.S. Swaminathan School of Agriculture, Centurion University of Technology and Management, Paralakhemundi, Gajapati, Odisha, India

#### Siddhartha Mukherjee

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal, India

#### Jaison M

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal, India

#### **Bishnu Prasad Dash**

Department of Agricultural Chemistry and Soil Science, Bidhan Chandra Krishi Viswavidyalaya, Mohanpur, West Bengal, India

#### Mehjabeen

Department of Soil Science and Agricultural Chemistry, Bihar Agriculture University, Sabour, Bihar, India

Corresponding Author: Shiva Kumar Udayana M.S. Swaminathan School of Agriculture, Centurion University of Technology and Management, Paralakhemundi, Gajapati, Odisha, India

### Nutrient biogeochemistry of coastal soils

## Puja Singh, Shiva Kumar Udayana, Siddhartha Mukherjee, Jaison M, Bishnu Prasad Dash and Mehjabeen

#### Abstract

The interface between land and ocean is termed as coastal zone and possesses specific features like highly dynamic nature, heterogeneity, diversity and productivity, fragile and sensitivity ecological sites as it belong to the transition zone. Coastal areas are rich in natural resources, which attract human settlement. The availability of light limits primary productivity here and is highly valuable as well vulnerable earth's habitat. Bacterial denitrification is a significant process in the coastal zone that plays an important role in organic C degradation primarily occurring in muddy sediments. It necessitates a lot of organic matter, a limited supply of oxygen, and a nitrate source. It's difficult to correctly estimate the rate of denitrification in sediments, especially when it comes to coupled nitrification-denitrification, in which organic matter decomposes to ammonium, which is then oxidized to nitrate, which is then denitrified. This paper deals with biogeochemistry of different nutrients *viz*. carbon nitrogen, phosphorus and sulphur and role of microbes in regulating different nutrient cycles.

Keywords: Coastal areas, transition zones, biogeochemistry, nutrient cycles

#### Introduction

The Coastal Zone is the area where the land meets the sea covering shoreline environment and coastal water or is a transition zone between land and oceans where diverse elements in the form of sediments collected from numerous sources such as rivers, seas, and atmosphere. River deltas, coastal plains, marshes, beaches, reefs, mangrove forests, lagoons, and other water components that deposit sediment before reaching to the sea allow numerous biogeochemical processes taking place beneath deposited sediment. Natural activities in coastal environments shape the vegetation and habitat of the organisms that live there. The significant degree of natural variability and diversity that exists in this area is owing to constant changes in its physical, chemical, and biological features as a result of changes in wave and current regimes, climate, and morphological processes. Coastal areas are rich in natural resources, which attract human settlement. Within 60 km of the shore, about half of the world's population reside. People are still migrating from inland to seaside locations at a breakneck speed. The fortes of the coastal zones are as follows:

- Highly heterogeneous and dynamic nature due to unstable physical, chemical, biological, physiographic and geological properties.
- Highly productive and diverse habitat (shelter large number of marine organisms and species).
- River deltas, coastal plains, marshes, beaches, reefs, mangrove forests, lagoons are considered under this area.
- Absorbs nutrient toxicity, sediments, and other wastes that could be classified as possible contaminants.
- Fragile and sensitive ecological sites (poor soil development) with location-specific factors such as salinity, acidic soil, sandy texture, and anaerobiosis. Location specific problems that predominating in India are: *viz.* sea-water intrusion in unbunded low-lying areas, iron toxicity in Orissa, impeded drainage in coastal Andhra Pradesh and Tamil Nadu along the east coast as well as in parts of Kerala and Gujarat along the west coast, highly permeable sandy soils in parts of Gujarat, and highly leached low-fertility lateritic soils with severe erosion problems along with undulating topography in some parts of Maharashtra, Goa, Karnataka and Kerala. Soils of Lakshadweep Islands are primarily coral sandy, calcareous and alkaline, whereas those of the Andaman and Nicobar group of islands are acidic, as well as poor in organic matter and available phosphorus (Ray *et al*, 2014).

Due to high nutrient loss, particularly in saline and alkaline soils (via volatilization) and also in deeply wet places, crop nitrogen recovery is relatively low (by leaching and run-off). The following are the major factors limiting crop growth in the coastal plains

- 1. Soluble salts and alkalinity build up in the soil,
- 2. Predominance of acid sulphate soils,
- 3. Periodic inundation of soil surface by tidal water,
- 4. Accumulation of salts and sediments by natural calamities such as tsunami and cyclone,
- 5. Eutrophication and hypoxia;
- 6. Shallow saline ground water. Nitrogen is being lost in large amounts due to volatilization, leaching, and run-off. In coastal acid sulphate or acid saline soils, phosphorus shortage is also a prevalent occurrence.

### Biogeochemistry of different nutrients and role of microbes in coastal region

Tidal wetlands are one of the most important global carbon pools because of their effective carbon sequestration capability (0.0426 Gt y<sup>-1</sup>), as well as inputs from upriver and tidewater (Chmura *et al.*, 2003) <sup>[13]</sup>. Luo *et al.* (2017) <sup>[24]</sup> observed that the availability of sulphate increases as salinity rises, whereas other electron acceptors, such as oxygen, nitrate, ferric oxides, and carbon dioxide, may rise briefly but then diminish as salinity and inundation rise. Because of the shifting electron acceptor pattern, microbial sulphate reduction may take precedence over other carbon mineralization processes. Sulfate enrichment, increased ionic and osmotic stress, decreased oxygen concentrations and redox potential, among other biogeochemical changes, all have an impact on organic carbon mineralization.

Repeated flooding in coastal areas deposit organic carbon and different nutrients making this fragile and sparse region highly productive. Microbes residing here act as "Biological engine" as playing a crucial part of the whole nutrition cycle and transformation (Azmi and Chatterjee, 2016)<sup>[6]</sup> such as fixing atmospheric nitrogen, solubilizing phosphates, producing ammonia, and triggering release of `the plant regulators. Halophiles and halotolerant growth microorganisms of this region produce hydrolytic enzymes such as amylase, nucleases, phosphatases, and proteases. These enzymes are involved in protein denaturation (Ventosa and Nieto, 1995) [40], as well as the generation of polyketide synthases (enzymes involved in the biosynthesis of secondary metabolites of erythromycin, rapamycin, tetracycline, lovastatin, and resveratrol). Riverine and groundwater inputs, atmospheric inputs, benthic interactions of nutrients (including denitrification), sediment suspension, upwelling, and sediment burial are all biogeochemical processes that environments. Many affect coastal biogeochemical transformations are mediated by microbes, in which electrons are shuttled from an electron source (e.g., organic molecules) to a terminal electron acceptor (TEA) via a complicated set of reduction-oxidation (redox) reactions, resulting in free energy that drives metabolic processes. Discussing various nutrient cycle in coastal areas are important as plant primary production is stimulated by various nutrient. E.g. Nitrogen boosts primary producers' carbon fixation, while phosphorus may impact heterotrophs' carbon turnover. Because nitrogen fixation is energy-intensive and typically limited by the availability of adequate carbon substrates, adding glucose to marsh sediments increased endogenous heterotrophic nitrogen Phosphorus-mediated fixation rates. reduction in heterotrophic nitrogen fixation observed it is most likely a function of secondary carbon limitation. Sulfate reduction is the major anaerobic metabolic route in seawater with salinities greater than 10 ppt (Sundareshwar *et al.*, 2003) <sup>[35]</sup>. Additional  $SO_4^{2-}$  may be unlikely to induce large changes in microbial community composition once the sulphate limitation threshold has been exceeded (Borruso *et al.*, 2014) <sup>[8]</sup>.

Biogeochemical study of an ecosystem reveal how high is productivity of the system in low-nutrient region, and how this sustains a diverse food web. The study identified other sources of nutrients input including rain, groundwater, nutrient recycling through sediments, sporadic mixing events through internal waves, and endolithic upwelling. Atkinson, M. J. (2011) <sup>[5]</sup> pointed nutrient concentration in coastal region change only little as water travels through shallow reefs, despite the fact that various habitats and zones appear to have varied quantities of nutrient production and consumption. The explanation for this was that if productivity was low overall, then one would expect to find little change in nutrients. The biogeochemistry of different nutrients is discussed below:

#### 1. Carbon cycle

The amount and fate of organic matter in coastal areas varies greatly, as it is influenced by local redox conditions (Friesen et al., 2018)<sup>[15]</sup>. Lack of oxygen under water logged condition in coastal areas impairs carbon mineralization resulting to high organic matter content accumulation and high productivity of the areas (Behera et al., 2014; Dutta et al., 2017) <sup>[7, 14]</sup>. Anoxic or sub-oxic conditions observed in the non-surface layers of coastal soil are often associated with sulphate or nitrate reduction (Varon-Lopez et al., 2014) [38]. Sulfate reduction is the most important respiration activity in mangrove sediments, accounting for more than 75 percent of mineralization. Increased salinity promotes the total mineralization of organic matter and the release of NH4+ as thermodynamically favourable metabolic pathways, such as Fe(III) or SO<sub>4</sub><sup>2-</sup> reduction (Gao *et al.* 2014) <sup>[16]</sup>. Salinity has been reported to increase, decrease, or have no effect on organic matter decomposition in wetlands, according to the literature.

#### 2. Nitrogen cycle

In marine environment because of high salinity a major portion of energy synthesized in microbial body is used in osmolyte production and the limiting oxygen concentration rather than complete nutrient mineralization favor fermentation where scanty of ATP is generated. Heterotrophic bacteria nitrogen fixation can be regulated by environmental conditions such as the presence of oxygen or a combined nitrogen and carbon source. Nitrogen-fixing bacteria may obtain nutrients from a variety of substrates found in coastal habitats, rather than relying on carbon and phenol concentrations (Pelegri and Twilley, 1998) [26]. Low N2 fixation happens in marine water due to a lack of energy sources. Microbial N<sub>2</sub> fixation adds new N to the system by converting atmospheric N<sub>2</sub> to organic N. While mineralization regenerates N internally, microbial N<sub>2</sub> fixation introduces new N to the system by converting atmospheric  $N_2$  to organic N. Due to sulphide inhibition of nitrifying bacteria (Joye and Hollibaugh, 1995) <sup>[19]</sup>, nitrification reduces with greater exposure to salt water (Noe et al. 2013) [25]. Small increases in salinity (EC from 1,100 to 16,000 lS/cm) can drive

nitrification in saline soils in the absence of increasing sulphide, but extremely significant increases (EC 16,500IS/cm) eventually hinder nitrification (Ardo n *et al.* 2013)<sup>[4]</sup>. Denitrification uses NO<sub>3</sub> as the TEA to convert NO<sub>3</sub> to N<sub>2</sub>. Nitrification offers an oxidized substrate for denitrification.

In the nitrogen cycle, nitrate molecules dissolved in mangrove mud are transformed by bacteria from nitrogenous organic compounds to ammonia. Denitrification is highly high in regions where wastewater is discharged, indicating a favourable environment for microbial growth (Rivera-Monroy et al., 1995) [30]. Some nitrogen-fixing bacteria, such as Azotobacter and Clostridium species, are abundant in ecosystems and play an important role in nitrogen enrichment (Sahoo and Dhal, 2009)<sup>[31]</sup>. Microbes fix 40-60% of the annual nitrogen demand at the rhizosphere and surface sediments level (Holguin et al., 2001) [18]. Different kinds of nitrogen-fixing bacteria were isolated from mangrove habitats, including some of the most important species such as Azospirillum, Azotobacter, Rhizobium, Klebsiella, and Clostridium. The quantity of Acidobacteria was strongly correlated with NH4+-N. Gemmatimonadetes, on the other hand, showed a substantial positive connection with NO3-N and a significant negative correlation with catalase (Tianyun Shaoa, et al., 2019) <sup>[34]</sup>.

#### 3. Phosphate solubilization

In coastal areas submergence of soil reduce Fe(III) to Fe(II), increasing iron concentration in soil causing precipitation of P along with Fe (Sengupta and Chaudhuri, 1991; Holguin et al., 2001) <sup>[18]</sup>. As a result, the phosphate content drops dramatically, resulting in nutritional insufficiency. Anaerobic bacteria prefer nonsoluble phosphate dissolution. Vazquez et have thoroughly discussed bacteria's phosphateal. solubilizing capability (2000). A vast variety of organic acids (lactic, fumaric, gluconic, succinic, and acetic acid) are produced during the phosphate solubilization process. These organic acids operate as chelators, binding to metals and removing phosphorus, allowing metals to be displaced (Vazquez et al., 2000) [39]. Atrophaeus, Paenibacillus macerans, Vibrio proteolyticus, and Xanthobacter agilis are some of the newly identified bacteria PSM. For saltwater and marine sediments, Bacillus spp. and Vibrio spp. have the potential to solubilize phosphate (Promod and Dhevendaran, 1987) <sup>[27]</sup>. In P cycling, the connection between S and Fe cycling is crucial. The dissolution of Fe-PO<sub>4</sub><sup>3-</sup> minerals and the release of PO43- result from the reduction of Fe(III) to ferrous iron [Fe(II)] and complexation with sulphide (Reddy and DeLaune, 2008) <sup>[28]</sup>. Following saltwater intrusion, ironsulfur complexation releases lasting weeks to months, potentially contributing to eutrophication of overlying and downstream streams (Lamers et al., 2002)<sup>[22]</sup>.

#### 4. Sulphate reduction

In mangrove ecosystem sediments, sulphate reduction can occur both aerobically and anaerobically (Kristensen *et al.*, 2008) <sup>[20]</sup>. It accounts for 75-125 percent of overall mineralization and is one of the most essential respiration processes (Alongi, 2014) <sup>[2]</sup>. The majority of microorganisms in mangrove sediments are anaerobic, although there is a small layer of an aerobic zone inhabited by aerobic microorganisms. Microorganisms in the aerobic zone can generally undergo aerobic respiration while degrading organic matter, whereas anaerobic degradation occurs by sulphate

reduction (Algoni, D. M., 2005)<sup>[1]</sup>. Mineralization is aided by the reduction of sulphate caused by organic matter breakdown (Alongi *et al.*, 1998)<sup>[3]</sup>. Sulfate-reducing bacteria create soluble sulphate molecules such as H<sub>2</sub>S and HS during the sulphate reduction process. These soluble sulphates combine with iron(I) and iron(II) to form pyrite (FeS<sub>2</sub>). Sulfur cycle is intertwined with Fe cycling, which is fueled by both biotic and abiotic interactions (Burgin *et al.*, 2011)<sup>[12]</sup>.

Sulfide can either directly impede denitrification by blocking the reductase enzymes that catalyse the final steps of denitrification, resulting in incomplete denitrification to NO<sub>2</sub>, NO, or N<sub>2</sub>O (Brunet and Garcia-Gil, 1996) <sup>[9]</sup>, or indirectly by inhibiting nitrification, reducing NO<sub>3</sub> availability. Increased ionic strength can also cause denitrification enzymes to malfunction (Laverman *et al.*, 2007) <sup>[23]</sup>. The utilisation of H<sub>2</sub>S and FeS as electron donors can also induce substantial denitrification, but only in the presence of enough NO<sub>3</sub><sup>-</sup> so if nitrification is hindered, no rise in denitrification is expected (Burgin and Hamilton, 2007, Burgin *et al.*, 2012) <sup>[11, 10]</sup>. Both nitrification and denitrification can be inhibited by high Cl concentrations, but microbial populations appear to be able to adapt to high amounts over time (Hale and Groffman, 2006) <sup>[17]</sup>.

Sulfide (H<sub>2</sub>S, HS, S<sub>2</sub>) is formed when sulphate is reduced, and it is harmful to many organisms (Lamers et al., 2013)<sup>[21]</sup>. Iron [Fe(II)] and reduced sulphur (e.g., H<sub>2</sub>S) mix abiotically to generate iron monosulfide (FeS) and, eventually, pyrite (FeS<sub>2</sub>) (Rickard and Morse, 2005; Tobias and Neubauer, 2019)<sup>[29, 36]</sup>. In wetland soils, salinization generally increases the concentration of Fe-S minerals (Schoepfer et al., 2014)<sup>[32]</sup>. Iron can act as a "buffer," preventing the development of reduced S molecules in porewater and the toxicity that comes with it (van der Welle et al. 2006; Schoepfer et al. 2014)<sup>[37,</sup> <sup>32]</sup>. Sulfate reduction is the major anaerobic metabolic route when seawater salinities are more than 10 ppt. Additional SO<sub>4</sub><sup>2-</sup> may be unlikely to induce large changes in microbial community composition once the sulphate limitation threshold has been exceeded. H<sub>2</sub>S concentrations are higher in systems with high organic matter (electron donor) levels, whereas S is pyritized in Fe-rich systems, resulting in  $FeS_x$ production and low pore water H<sub>2</sub>S buildup.

#### 5. Conclusion

The ecogeomorphic and ecological classifications of mangrove wetlands are clearly delineated by natural boundaries. Geophysical processes across different geomorphological settings and their interaction with ecological processes that are regulating the diversity in mangrove community structure and ecosystem function ultimately control biogeochemistry of different nutrients. In addition, climate, landform and other basic characteristics of a coastal region together with local geophysical processes also have influence on altering nutrient cycles. Thus studying nutrient biogeochemistry of coastal soil and how it differ from terrestrial land is vital important.

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