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# Sulfur Emission from Indian Ocean and Role of Microbial Communities

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*Abstract:* **Ocean which forms the ¾ part of Earth plays a very vital role in major biogeochemical cycle like sulfur, phosphorus, carbon etc. Among the entire biogeochemical cycle, ocean forms the originator of sulfur cycle. Ocean is basically comprises of thousand meter thick mat of sediment which harbor's lakhs of microbes. These microbes use sulfur for energy generation, synthesis of organic material, growth and metabolism, during which the sulfur is converted into different redox form. Sulfur transformation which begins with sulfate reduction is interconnected with other biogeochemical cycle also, thus effecting abiotic as well as biotic communities in the ecosystem. The microbes involved in this, have diverse genetic, metabolic, physiological features for fulfilling their role in the ecosystem. In this context we get a glimpse of how ocean forms the source and sink of sulfur and the role of microbes involved in it. The study comprises the emission and circulation of sulfur in Indian Ocean system.**

***Index Terms:*** **sulfur, chemoautotrophs, hydrothermal vents, sulfur cycle, DMS, DMSO, reduction-oxidation**

## I. INTRODUCTION

Sulfur is one of those essential elements whose circulation in nature is critically dependent on microbes. It is considered as the $10^{th}$ most abundant element in the universe. The sulfur cycle referred as the movement of sulfur from exosphere and biosphere. In sulfur cycle Oceans is considered as the major source of sulfur, in which it exist in variety of valence state from -2 in sulphide or reduced organic sulfur to +6 in sulfate . Sulfate is considered as the most stable form in oxic environment whose major source are weathering and leaching of rocks and sediment. Sulfur is also present in reduced state of -2 or 0 as in the elemental form in the anoxic environment. The major source of sulfur emission in Indian oceans is deep sea hydrothermal vents, sea spray and microbial communities. This sulfur cycle include important process such as the incorporation of sulfur into biomass of ocean and reverse process of mineralization of organic sulfur compounds after aerobic and anaerobic decay of dead phytoplankton and other organism. This sulfur cycle is mostly evaluated from the data of the carbon cycle in the ocean. The former line can be proven by one example , let us assume that the yearly primary production of organic matter in ocean is nearly 36,000Tg ,and if we consider that the sulfur content of phytoplankton is one percent in the whole biomass , then about 360Tg of sulfate of ocean is accumulated by living being. After death and decay only 10 % of organic matter reach to the bottom, from this we can say that the flux of organic sulfur to sea bottom is 36 Tg per year, and flux of mineralized sulfur of dead marine plants and other organism is estimated around 324Tg per year. Apart from this, sulfur cycle is also interlinked with oxygen, nitrogen etc. because during the interconversion of sulfur into other form it combine with oxygen, nitrogen and with varied metals like iron, calcium in form of pyrite and sulfate near the mixing zone like mid ocean ridge, hydrothermal vents, plumes etc. where the new oceanic crust develops by mixing of mantel fluid with marine water. In the following way the transmission of sulfur is followed via ocean to ecosystem.

## II. SOURCE OF SULFUR IN MARINE ECOSYSTEM

The sulfur cycle in the ocean begins from the deep sea hydrothermal vents .Hydrothermal vents are the place of active volcanic activity in oceanic crust mostly near mid oceanic ridges. In the hydrothermal vent, metal sulphide ore, sulfate, hydrogen sulphide are produced naturally due to interaction of rocks and sea water at very high temperature. At deep sea hydrothermal vents, sulfate is precipitated out from seawater in form of anhydrite along with that hydrogen sulphide is produced due to leaching of sulfur from basalt at temperature above 400 Celsius in oceanic crust. This hydrogen sulphide is also produced by reduction of sulfate compounds from seawater. As the hydrothermal fluids are rich in hydrogen sulphide, so this become a high productive ecosystem for microbes like chemolithoautotrops, who eventually mediate the sulfur cycle through dissimilatory sulfur metabolism and mediate the tropic transfer. Apart from this on the continental shelf the sulfate reduction contribute to the degradation of organic matter, because of this hydrogen sulphide is produced which is then re oxidized by sulfur oxidizing bacteria such as Thiomargarita namibiensis. We are aware that as the light does not penetrate under deep zones, so there the vent becomes a type of chemosynthetic based ecosystem where primary productivity is fuelled by chemical compound as a source of energy. Along with that the preference for the neutral PH range favors the facultative chemoautotrophs in the well buffered seawater. This biochemical versatility of sulfur bacteria along with the relatively high concentration of reduced sulfur becomes the major condition for their predominance in the vents. As this vent are further rich in dissolve mineral and thus the microorganisms use sulfur compound like hydrogen sulphide for production of organic material through the process of chemosynthesis.

There are various steps involved in sulphur cycling through which sulphur is converted into different redox state:

- Organic sulphur is converted into inorganic sulphur compounds like hydrogen sulphide, elemental sulphur, and sulphide mineral.
- Hydrogen sulphide, sulphide and elemental sulphur like compounds are oxidized to form sulphate.
- Sulphate is reduced to form sulphide compounds.
- Phototrophic sulphur oxidizers, Chemolithotrophic sulphur oxidizers, sulphur reducers, sulphate reducers and organic sulphur utilizers like microbes incorporate sulphide into organic compounds.

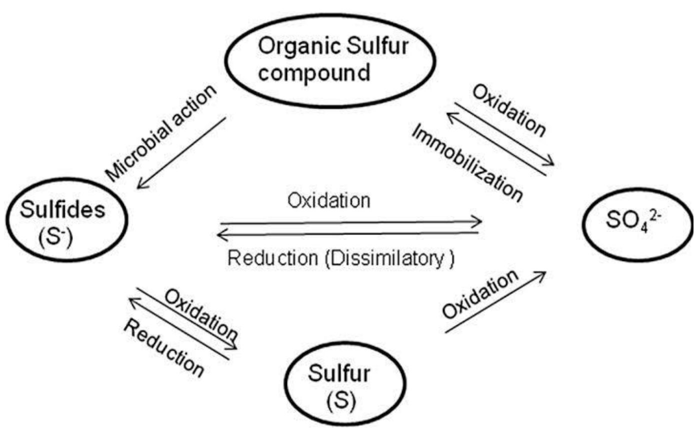


**Fig: 1 interconversion of sulfur through redox Reaction**
(Bikash chandra behera, 1999)

## III. EMISSION OF SULFUR FROM INDIAN OCEAN

In Indian Ocean the major source of sulphur emission are the major hydrothermal vents like Dodo, Solitaire, Edmond, Karrie, the former are present off axis while the later are present in the axis. These vents are majorly black smoker, which are major emitter of sulphide in the ocean. Apart from major vents there are tectonically active regions, plumes etc., which are involved in emission of sulphur compounds by sediment bed and mantle interaction. In these region thermococcus, pyrococcus represent the most abundant cultivated population. Methanococcales, aquifex, Persephonella, epsilon proteobacteria, hydrogenimonas, and sulfurimonas are thiotrophic chemolithoautotrops while Archaeoglobus, Thermodesulfatator are abundant sulfate reducing chemolithotrophs. Apart from the vents the circulation of sulfur is mediated in marine sediments by some sulfate reducing prokaryotes via dissimilatory sulfate reduction (DSR) to sulphide through anaerobic respiration. Because of this, sulphide is also produce inside them. This is mainly occurring in bacteria such as Beggiatoa, Thiopleca, and Thiomargarita. These bacteria also use nitrate and phosphate for oxidizing sulphide of the sediments. In sedimentary habitat Dimethyl sulfide (DMS) is also produce in the anoxic condition by methylation of sulphide and methanethiol. Then this DMS is used up by both aerobes as well as anaerobes. This sulfur is released from ocean to terrestrial part in the form of DMS and ahead gets converted into other forms for continuing sulfur cycle. Sometimes the sulphide is deoxidize back to sulfate by different intermediative process which involves oxygen, nitrogen, manganese, iron where by some sulphide precipitates and buried in sea beds. The DMS produced by microbes is released into atmosphere and serve as condensation nuclei, resulting into cloud formation and conversion into sulfur dioxide. Sulfur enters the atmosphere and biosphere directly in the form of hydrogen sulphide. Apart from this the sulfate salt enters from ocean to the atmosphere by sea spray near the continental shelf. In this way sulfur enter the other sphere from ocean.

## IV. PHYTOPLANKTON ROLE IN SULFUR CYCLE IN PHOTIC ZONE OF INDIAN OCEAN

The sulphide compound released in oceanic crust during emission from hydrothermal vents is majorly incorporated by bacteria, archaea but apart from this sulfur is also incorporated in the phytoplankton through assimilatory uptake of sulfate in oxidize or some into sulfate polysaccharide and some assimilated into amino acid like methionine and cysteine. This assimilated form is then converted into other forms like DMSP, DMS etc. For instance methionine like amino acid is converted into a more stable form commonly referred as Dimethyl sulfoniopropionate (DMSP). The DMSP is then getting converted into Dimethyl sulphide (DMS), Acrylic acid by some enzyme present in phytoplanktons and some amount is converted by sulfur bacteria. This DMS is majorly consumed by many bacteria and converted it into Dimethyl sulfoxide a non volatile product and sulfate, the common bacteria involved are methylophaga .The DMS is oxidize into many other form by marine ecosystem such as into sulfur dioxide, dimethyl sulfoxide(DMSO), dimethyl sulfone, methane sulfonic acid and sulphuric acid. Moreover some bacteria use the DMSP and instead of converting it into DMS and acrylic acid they carry some other pathway were DMSP is converted into Methiolpropionate and methanethiol. This methanethiol is then oxidizing into sulfur amino acid such as methionine. It is estimated that DMSP accounts for more than half of the sulfur requirement for heterotrophic bacterial biomass as well as phytoplankton's. This phytoplankton then carries this sulfur compound to upper tropic level. Among all this only 2-3% of DMS is released to atmosphere from the ocean. This is how the sulfur released from ocean is incorporate into life through oxidation pathway.

**Table 1: types of archaea and bacteria involved in sulfur cycle in ocean**

| **Archaea** | |
|---|---|
| 1.Crenarchaeota | 2.Euryarchaeota |
| • *Thermoproteoles*<br>• *Desulfurococcales*<br>• *Sulfolobales* | • *Archaeoglobales*<br>• *Thermococcales*<br>• *.Thermoplasmatales*<br>• *Methanogens* |
| **Bacteria** | |
| 1.Proteobacteria<br>2.Chlorobiaceae<br>3.Firmicutes<br>• *Desulfotomaculum*<br>• *Desulfosporosiunus*<br>• *Ammonifex*<br><br>4.Nitrospiraceae<br>• *Thermodesulfovibrio*<br><br>5.Aquificae<br>• *Aquifex*<br>• *Persephonella*<br>• *Desulfurobacterium*<br>• *Thermovibrio*<br>• *Balnearum*<br>• *Sulfurihydrogenidium*<br><br>6. Chloroflexaceae<br>• *Chloroflex*<br><br>7. ThermodeSulfobacteriaceae<br>• *Thermodesulfatator*<br>• *Thermodesulfobacterium* | |

**Table 2: types of proteobacteria involved in sulfur cycle in ocean**

| **Proteobacteria** |
|---|
| α – proteobacteria |
| • *Roseobacter*<br>• *SAR-11*<br>• *Paracoccus*<br>• *Rhodobacter*<br>• *Rhodospirillum*<br>• *Rhodomicrobium* |
| β– proteobacteria |
| • *Thiobacillus*<br>• *Thiomonas*<br>• *Alcaligenes*<br>• *Rubrivivax*<br>• *Rhodocyclus*<br>• *Rhodoferax* |
| γ– proteobacteria |
| • *Thiomicrospira*<br>• *Beggiatoa*<br>• *Thioploca*<br>• *Thiomargarita*<br>• *Riftia*<br>• *Calyptogena*<br>• *Methylophaga*<br>• *Pseudomonas*<br>• *Chromatiaceae*<br>• *Ectothiorhodospiraceae* |
| δ– proteobacteria |
| • *Desulfovibrio*<br>• *Desulfotalea*<br>• *Desulfonema*<br>• *Desulfosarcina*<br>• *Desulfuromonas*<br>• *Desulfurella*<br>• *Desulfuromusa*<br>• *Geobacter*<br>• *Desulfovibrio* |
| ε– proteobacteria |

- *Arcobacter*
- *Thiovulum*
- *Sulfurimonas*
- *Sulfurovum*
- *Sulfurospirillum*
- *Nautilia*
- *Caminibacter*

## V. MICROBIAL CONTRIBUTION IN SULFUR CYCLE IN INDIAN OCEAN

Microbes are the major contributor of sulfur cycle in the ocean. Different types of microbe are found near vent, plumes, lower crust and well as on the upper sediment, facilitating interconversion through various processes such as:

•*Anaerobic oxidation*: In this process the sulfate reduction is carried out along with oxidation of methane anaerobically by methaneotrophic archaea, which convert the sulfate into zero valent sulfur. Some delta bacteria Desulfovibrio, Desulfotale, Desulfonema reduce the sulfate into sulphide.

•*Dissimilatory reduction of sulfur cycle intermediate*: It is carried out anaerobically in which sulphide is formed by reduction. This is then further oxidized into sulfate. Example includes ammonifex, Nautila, Desulfuromonas.

•*Sulfur oxidation:* Sulfur oxidation metabolism is restricted to the upper sediment layer. Various microbes involved are; beggiatoaceae, this bacteria stores elemental sulfur to bridge the gap between oxygen and sulphide. Another is Thioplaca, it glides between oxic and sulphuric sediment layer to replenish the sulfur reservoir.

•*Disproportionation of inorganic sulfur compound*: It is basically performed by anaerobes where the sulfur cycle intermediate acts as electron donor as well as acceptor. Example: delta proteobacteria, gamma proteobacteria, Thermodesulfo bacteria, Firmicutes.

•*Organo sulfur molecule transformation*: It include the conversion of organic sulfur such as methionine, cysteine, co enzyme, co factor, sulfonate and sulfate. This are assimilated into saccharide, lipids, flavanoids etc. Examples: Rhodopireleula, Methanogens, SAR – 11, Alcaligenes.

The sulfur cycle get reversed while going through the dissimilatory sulfate reduction pathway, where the sulfate get reduced by reducing bacteria or inorganically by thermo chemical sulfate reduction path . The sulfate of organic compound is reduced to hydrogen sulphide, which was the initial substrate of our oxidation pathway. Moreover it is estimated that on the global scale the remineralization of the organic matter into sulfur is around 29%, which is found to be deposited to the seafloor with the help of sulfate reducing microbes. This is considered as the end product of the anaerobic microbial food web. In one study it is also estimated that around 11.3 teramole of sulfate is reduce to hydrogen sulphide and this hydrogen sulphide and other reduced sulfur serve as the electron donor for the sulfur oxidizing microbes (SOM) which further continue the sulfur transmission in ecosystem.

All the pathways of interconversion of sulfur can be linked to one another as:

1) *Aerobic:* Hydrogen sulphide is converted into elemental sulfur by oxidation and elemental sulfur is converted to sulfate via oxidation of sulfate. The sulfate gets converted into amino Acid via assimilation sulfate reduction and desulphurylation of amino acid leads to again conversion into hydrogen sulphide.

2) *Anaerobic:* In the absence of oxygen the hydrogen sulphide is transformed into elemental sulfur inside phototrophic bacteria through oxidation, this elemental sulfur gets oxidized into sulfate at the end. Sometimes the sulfate is converted into elemental sulfur through dissimilatory sulfate reduction, following this pathway the elemental sulfur is again get converted into hydrogen sulphide. On the other hand through the assimilatory sulfate reduction pathway the sulfate get incorporated into amino acid and this amino acid is transformed into hydrogen sulphide through desulphurylation. This is how the interconversion of the sulfur is incorporated whose main vector are the microbe.

**Table3: amount of sulfur by various processes**

| species | Amount |
|---|---|
| Lifetime of S in water column in the ocean | Year |
| Sedimentation of Sulfur as particulate S from water column (R) | 0.9-1 umol m-2 d-1 |
| [SO4-2] in ocean water | 28.9/mm |
| C:N: S in cultured marine phytoplankton | 124:16:1.3 |
| C:N: S in marine particulate matter | 182:27:1 |
| Sulfur assimilated by marine phytoplankton each year | 1320Tg S/yr |
| DMS global emission over the ocean | 15.5 Tg S/yr |
| DMS global emission over land | 1.1 Tg S/yr |
| DMSP as percentage of total particulate organic Sulfur in the ocean | 22% |
| DMS as percentage of total particulate organic Sulfur in the oceans | 0.9% |
| DMS from DMSP as percentage of total SO, assimilation | 29% |
| SO4-2 sulfur assimilated released to atmosphere | 0.3% |
| [DMS] in surface seawater in winter | 0.2nmol/lit |
| [DMS] in surface seawater in summer | 10nmol/lit |
| [DMS] in plankton blooms | >90nmol/lit |
| DMSP biological turnover in non bloom conditions | 3-130nmol/lit/day |
| DMSP : DMS ratio in the ocean | 3:25 |
| DMSP diverted towards methanthiol production | 70-95% |
| Organic Sulfur as DMSP in algal cells | 70% |
| Rate of SO assimilation by phytoplankton | 260umol/m sq/day |
| Sulfur assimilated into low molecular weight compounds by phytoplankton | 40% |
| S assimilated into proteins by phytoplankton | 35% |
| Sulfur assimilated into ester-sulfate by phytoplankton | 21% |

## VI. CONCLUSION

The sulfur cycle majorly depends on the activities of metabolically and phylogenetically diverse microorganisms, maximum of which resides in the deep oceans. The sulfur rarely becomes a limiting factor but their turnover plays a very vital role in maintaining the ecosystem. Inorganic sulfur is critically important for chemosynthesis in deep sea where the light source is unavailable, while the organic sulfur plays a crucial role in microbial metabolism in the upper water column. This sulfur metabolizing microbes also plays a vital role in maintaining the tropic transfer and degradation of the biomass. This microbe also increases the ecosystem productivity by retaining the nitrogen, phosphorus and other elements. Along with maintaining microbial communities, it also plays a crucial role in climate regulation. Sulfur circulation is also linked with other biogeochemical cycle. Even a slight change in the phytoplankton and bacterioplankton or sulfur cycle can create a diverse effect on the global system.

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