# Spatial variability of biochemical composition in coral reef sediments of Kavaratti and Pitti islands, Lakshadweep archipelago

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In this study, variability of biochemical composition in the surficial coral reef sediments of Kavaratti and Pitti islands in Lakshadweeep archipelago was investigated. Biochemical composition of sedimentary organic matter from the study area was characterized by the dominance of proteins in Pitti and carbohydrates in Kavaratti over lipids. The percentage ratio of the labile to total organic matter indicated that most of the deposited organic matter was refractory in both environments. The higher PRT:CHO ratios in Pitti sediments compared to that of Kavaratti indicated that in the former there was low dead organic matter accumulation. The lower LPD:CHO ratios estimated for sediments in both islands indicated low quality of labile organic matter to support benthic fauna.

[Keywords: Coral reef sediments, Kavaratti, Pitti, Organic matter, Biochemical composition, Labile organic matter]

## Introduction

Marine sediment overlay two-thirds of the earth's surface representing one of the largest microbial habitats on the earth. It is complex in nature and acts as the major sites for mineralization and nutrient regeneration of organic matter derived from pelagic primary production and terrestrial input<sup>1</sup>. The surficial sediments can play an important regulatory function through the storage and transformation capacity of organic matter and nutrients and through the reactivity of biogeochemical buffers<sup>2</sup>. A fraction of 25–50% of the organic matter derived from coastal primary production is deposited to the sediments<sup>3,4,5</sup>. The oxic surface layer of marine sediments can account for more than half of the total organic carbon mineralization<sup>6,7</sup>.

Coral reef ecosystems are widely recognized as among the most biologically diverse and complex ecosystems; they have been called the marine equivalent of tropical rain forests<sup>8</sup>. These are characterized by exceedingly high rates of productivity, yet are typically situated in nutrient poor waters<sup>9</sup>. Coral reef sediments are generally loose and unconsolidated in nature. Sediments are fundamental for the function of oligotrophic coral reef ecosystems because they are major places for organic matter recycling. This releases the nutrients to the surrounding environment and the dynamics of nutrients are linked to the ecological processes. The study of nutrients would help in understanding the potential availability of life supporting elements in the aquatic system<sup>10</sup>. Therefore, both qualitative and quantitative studies are important for understanding the basic processes governing the distribution and biogeochemical cycling of nutrients<sup>11</sup>. The best coral development is always found on the nutrient-depleted oligotrophic waters, as they are the least tolerant of nutrient enrichment. The biogeochemical processes in the oxic sediment layer play an important role for highly permeable, carbonate sediments in coral reefs<sup>12,13,14,15</sup>.

Reef sediments are typically derived from the calcareous skeletons of corals processed by bioeroding organisms, but also by other biological, chemical and physical processes<sup>16,17</sup>. Generally, permeable reef sediments function as biocatalytical filters that lead to a very effective processing and regeneration of organic matter<sup>18,19,20,21</sup>. Consequently, these sediments contribute to the release of the limiting nutrients N and P after remineralization of organic material<sup>22</sup>. Through their contribution to an efficient element cycling<sup>18,22</sup>, reef sediments are crucial for the functioning of coral ecosystems and help to maintain typically high biomass and primary productivity in coral reefs<sup>23,24</sup>, despite of the surrounding oligotrophic waters<sup>25,26,27</sup>. The diagenesis or the mineralization process occurring in sedimentary environments is associated with organic matter and therefore the characterization of organic matter is a prerequisite for biogeochemical studies. The biogeochemical processes associated with organic matter remineralisation are not a simple function of the total quantity of organic matter present, but also depend on the quality of organic matter. Therefore, the assessment of nature and quality of organic matter is of prime importance for explaining organic matter remineralisation.

Biochemical composition of sedimentary organic matter has been used to gather information on the origin and parameters controlling the diagenetic fate of organic matter<sup>28</sup>. The assessment of the quantity and quality of organic matter, whether labile or refractory, is a prerequisite for explaining diagenetic processes. The labile fraction of organic matter consists of mainly carbohydrates, lipids and proteins, which are assumed to represent a fraction of organic readily available matter more to benthic consumers<sup>29,30</sup>. In addition, the biochemical composition of sediments is being recently proposed for assessing the trophic status of coastal marine systems<sup>30,31</sup>.

The present study compares the spatial distribution of biochemical composition and nutrients in the coral reef sediments of an inhabited island, Kavaratti and an uninhabited island, Pitti belonging to Lakshadweep archipelago. The study also focuses on assessing the main sources and the nutritive value of the sedimentary organic matter in the study area.

## **Materials and Methods**

## Study area

Lakshadweep is an archipelago consisting of 12 atolls, 3 reefs and 5 submerged banks. It is located between 8°-12°13"N latitude and 71°-74°E longitude. It is 220-440 km away from the coastal city of Kochi in Kerala, India. Lakshadweep has an area of 32 km<sup>2</sup> and it has 10 inhabited islands.

Kavaratti: The Kavaratti island is the headquarters of the Union Territory of Lakshadweep, India. It lies between  $10^{\circ}32'$  and  $10^{\circ}35'$  N latitude and  $72^{\circ}35'$  and  $72^{\circ}40'$  E longitude, having an area of 4.22 km<sup>2</sup> and located at a distance of 404 km off Cochin. It is the second most populated island in Lakshadweep. The reef, which is situated on the western side of the island, encloses a lagoon in between the reef and island, having a length of about 6 km. The land is level to very gently sloping except for some elevational differences along the western lagoon side. The island is oriented in a NE-SW direction (Figure 1).

Pitti: Pitti is an uninhabited coral islet in the Union Territory of Lakshadweep. It is located at 10°46'N



Fig. 1 — Location Map of Kavaratti

72°32'E about 24 km to the north of Kavaratti, 37 km to the east of Agatti. The island is low, arid and is difficult to access, lacking adequate anchorage points. There is no lagoon enclosing the island. It is 300 x 200 m in size and devoid of vegetation. There is a dark rock on the eastern side and several stone cairns. Several pelagic birds nest on this island (Fig. 2).

# Sampling Procedure

Sediment samples were collected from different sampling sites around the shore, lagoon and outer lagoons of Kavaratti island and from the oceans of Pitti island belonging to Lakshadweep archipelago during May 2014 (Table 1). Surface sediment samples from the shore were taken in polythene bags using a clean plastic spoon and sediments from lagoon (at 3 m depth) and outer lagoon stations (at 20 m depth) were collected by scuba diving. These were kept in ice box for transportation to the laboratory and then stored in deep freezers till all the analyses were performed.

# Analytical techniques

Sediment pH was measured in suspension of 1:1 air-dried sediment-to-water ratio using calibrated pH



Fig. 2 — Location map of Pitti

meter. Organic carbon content in sediment was determined volumetrically by wet oxidation method as outlined by Walkley and Black (1934)<sup>32</sup> and then converted to organic matter according to Jackson  $(1958)^{33}$ . Keeney and Nelson's  $(1982)^{34}$  method was used for the extraction of nutrients. These were then estimated according to the procedure of Grasshoff et al., 1999.35

Spectrophotometric methods, using Thermofischer Scientific Evolution 201 UV Visible Spectrophotometer were employed for the determination of nutrients and biochemical composition in sediments. Protein (PRT) analyses were carried out following the procedure of Lowry et al. (1951)<sup>36</sup>, with albumin as standard. The amount of protein nitrogen was obtained by multiplying protein with a factor of 0.16<sup>37</sup>. Carbohydrates (CHO) were analysed according to Dubois et al. (1956)<sup>38</sup> using D-glucose as standard. Lipids (LPD) were analysed using Barnes and Blackstock (1973)<sup>39</sup> procedure using cholesterol as standard. All analyses were run on triplicates and the average values were reported.

The sum of all proteins, lipids and carbohydrates (LOM) was defined as labile or easily assimilable organic fraction<sup>40,41</sup>. Lipid, carbohydrate and protein were converted into carbon equivalents using 0.75, 0.40 and 0.49 mg C equ  $kg^{-1}$  conversion factors, respectively<sup>42</sup>. The biopolymeric carbon fraction (BPC) was calculated as the sum of carbohydrate,

1.

Table 1 — Sampling Locations								
S – Shore, L – Lagoon, O – Outer lagoon, P – Pitti								
Station	Landmark	Geographical Co-ordinates						
S1	Iceplant & Fisheries Jetty	10 <sup>°</sup> 34' 34.04" N 72 <sup>°</sup> 38' 21.04" E						
S2	Boatyard Jetty	10 <sup>°</sup> 34' 32.28" N 72 <sup>°</sup> 38' 20.3" E						
S3	Fish Processing Centre	10 <sup>°</sup> 34' 19.23" N 72 <sup>°</sup> 38' 14.67" E						
S4	Jetty	10 <sup>°</sup> 34' 16.36" N 72 <sup>°</sup> 38' 11.41" E						
S5	School	10 <sup>°</sup> 33' 32.16" N 72 <sup>°</sup> 37' 49.77" E						
S6	Chicken Neck	10 <sup>°</sup> 32' 48.29" N 72 <sup>°</sup> 37' 21.08" E						
S7	Helipad	10 <sup>°</sup> 32' 29.66" N 72 <sup>°</sup> 37' 7.02" E						
S8	Chicken Neck East	10 <sup>°</sup> 32' 44.52" N 72 <sup>°</sup> 37' 20.21" E						
S9	Secretariat	10 <sup>°</sup> 33' 29.09" N 72 <sup>°</sup> 38' 23.28" E						
S10	Light House	10 <sup>°</sup> 33' 38.65" N 72 <sup>°</sup> 38' 46.7" E						
S11	Administrative Bungalow	10 <sup>°</sup> 34' 36.86" N 72 <sup>°</sup> 38' 35.79" E						
L1	Jetty	10 <sup>°</sup> 34' 43.56" N 72 <sup>°</sup> 38' 2.25" E						
L2	Chicken Neck	10 <sup>0</sup> 33' 18.04" N 72 <sup>0</sup> 37' 0.69" E						
01	Entrance	10 <sup>0</sup> 34' 57.33" N 72 <sup>0</sup> 38' 3.7" E						
02	Helipad	10 <sup>°</sup> 32' 40.32" N 72 <sup>°</sup> 36' 41.72" E						
03	Secretariat East	10 <sup>0</sup> 33' 21.68 " N 72 <sup>0</sup> 38' 27.76" E						
P1	Eastern side	10 <sup>0</sup> 45'37.16" N 72 <sup>0</sup> 32'1.66" E						
P2	Southern side	10 <sup>°</sup> 46' 8.56" N 72 <sup>°</sup> 30' 55.07" E						
P3	Shore	10 <sup>0</sup> 46' 45.99" N 72 <sup>0</sup> 31' 56.88" E						

protein and lipid carbon<sup>29</sup>. The PRT: CHO and LPD: CHO ratios were also calculated to determine the quality of sedimentary organic matter.

# Data analysis

Data was subjected to statistical analysis to explore the possible associations existing between different variables and the analysis was carried out using the software package IBM SPSS Statistics 20. Pearson correlations were determined to find out the interrelations between different parameters. Statistical significance of the observed spatial variations in the analyzed sedimentary parameters of both islands was checked using one-way Analysis of Variance (ANOVA).

# **Results and Discussion**

Sedimentary pH varied between 8.01 and 8.8 in Kavaratti, whereas in Pitti, the range was between 8.15 and 8.29 (Fig. 3). Total organic matter in the sediments of Kavaratti ranged between 0.2928% and 1.0380%. Accumulation of organic matter is facilitated by slow decomposition in low-energy (characterized by low water current dynamics) fine-grained sediments<sup>43</sup>. Our findings of higher accumulation of organic material at Kavaratti, which was almost twice that of Pitti were supported by this low water current dynamics prevailing in the former island<sup>44,45,46</sup>. Especially calcareous reef sands are often associated with high numbers of heterotrophic microorganisms<sup>47</sup> involved in a rapid remineralization of organic matter<sup>18,22</sup>. As Kavaratti is enclosed by a

lagoon, it acts as a barrier in reducing tidal action and mixing and hence the lagoons of Kavaratti were rich in organic matter. Organic matter originates in these lagoons from autochthonous sources, such as phytoplankton, micro algae and aquatic macrophytes and also from allochthonous sources, such as terrestrial vegetation, freshwater marshes, numerous lines and patch coral reef communities and organic pollution from the upper parts of the hydrological basin. In Pitti, the organic matter ranged only between 0.1597% and 0.6920%, as it is an uninhabited island without a coral reef lagoon and is subjected to high water current dynamics when compared to Kavaratti (Figure 4).

The availability of inorganic nutrients has been implicated as the most important factor limiting the productivity of the coral reef ecosystem. Further, nutrient dynamics in the coral reef ecosystem is complex, since the corals are able to utilize the nutrients either from the sediments or from the water column. The average concentration of nitrite nitrogen, nitrate nitrogen, and inorganic phosphate in Kavaratti showed 0.9272, 16.3928 and 0.4629 mg/kg, respectively. In Pitti, the average concentration of inorganic phosphate (0.7324 mg/kg) was higher than Kavaratti, while the average concentrations of nitrite (0.8062 mg/kg) and nitrate (11.2901 mg/kg) were lower. As numerous pelagic birds were nesting in the island Pitti, the excreta of these birds (guano) might be an important source of inorganic phosphate and hence its average value was higher than that of Kavaratti. The spatial variations of inorganic nutrients in both islands are given in Figures 5 and 6.





The estimation of nutritional value of the sediment is accomplished with the help of biochemical indices like concentration of protein, carbohydrate, lipids, protein/carbohydrate ratio, and lipid/carbohydrate ratio<sup>30,48</sup>. The spatial distribution of biochemical components is shown in Figure 7. The mean concentrations of total carbohydrates ( $218.15 \pm 74.94$ ) mg/kg and total lipids (89.13  $\pm$  29.72) mg/kg were higher in the sediments of Kavaratti. In Pitti, the mean values of total carbohydrates and total lipids were  $(169.73 \pm 56.34)$  mg/kg and  $(67.25 \pm 3.22)$  mg/kg, respectively. But the higher concentrations of total proteins were reported from Pitti as  $(238.40 \pm 129.60)$ mg/kg. The organic biochemical components vary faster than the more conservative total organic carbon in response to spatial changes in the benthic trophic status associated to both natural and human-induced environmental alterations<sup>30,31,49,50</sup>

The labile organic compounds in sediments represent the fraction of organic matter available to the benthic



Protein-to-carbohydrate ratio (PRT:CHO) is used as an index to determine the origin of material present



Fig. 6 — Spatial variation of nitrate



Fig. 8 — Percentage distribution of biochemical composition

Pitti

in sediments and to distinguish between the presence of fresh materials and age of sedimentary organic matter<sup>40,41</sup>. Dominance of carbohydrates and lower PRT:CHO ratio (< 1) is a typical feature of detrital heterotrophic environments<sup>52</sup>. Since proteins are more readily used by bacteria than carbohydrates<sup>53,54</sup>, high PRT:CHO ratios indicate living organic matter or "newly generated" detritus<sup>40</sup> and the role of proteins as potentially limiting factor for the benthic consumers<sup>29</sup>.

The mean PRT:CHO ratio in Kavaratti was almost half the one of Pitti, reaching 0.8472 and 1.6107, respectively. The low values (on average < 1) in Kavaratti suggest that these sediments were characterised by a larger amount of aged organic matter<sup>55</sup>. As Pitti, a small uninhabited island without lagoon, is generally subjected to strong hydrodynamic conditions such as tidal action and mixing, it is more dynamic compared to Kavaratti. Compared to Pitti,

there is low water exchange in Kavaratti since the coral reef patches in the lagoon act as a barrier. This low hydrodynamic condition in Kavaratti favours the accumulation of sedimentary organic matter.

The lipid content and lipid-to-carbohydrate ratio (LPD:CHO) have been used as good indices to describe the energetic (food) quality of the organic contents in the sediments<sup>42,56,57</sup>. The estimated LPD: CHO ratio was less than 1 in both islands. This pointed towards the poor quality of labile organic matter to support benthic fauna in these islands. The spatial variation of biochemical ratios are given in Figures 11 and 12.

### Statistical analysis

analysis Pearson correlation showed that significant positive correlations were observed between total organic matter and inorganic nutrients like nitrite (0.05 level) and phosphate (0.01 level) in both islands. This showed that nutrient concentration



Fig. 10 — Variation of protein nitrogen

	14010 2 1	rube 2 reason conclusion matrix for the sectimentary parameters of Ravarati and Thu							
	pH	Nitrite	Phosphate	Nitrate	TOM	TCHO	TPRT	TLPD	
рН	1								
Nitrite	-0.378	1							
Phosphate	-0.101	0.247	1						
Nitrate	-0.090	0.658**	0.109	1					
ТОМ	-0.174	0.518*	0.694**	0.389	1				
ТСНО	0.201	0.252	-0.356	0.415	-0.115	1			
TPRT	-0.016	0.429	0.045	0.147	0.180	0.176	1		
TLPD	-0.220	-0.042	0.009	-0.424	-0.102	-0.062	-0.254	1	

Table 3 — One-way ANOVA results of sedimentary parameters of Kavaratti and Pitti

Parameter	Kavaratti	Pitti	p - value	
pН	$8.3144 \pm 0.2369$	$8.1967 \pm 0.0808$	0.416	
Nitrite	$0.9272 \pm 0.5334$	$0.8062 \pm 0.4498$	0.718	
Phosphate	$0.4629 \pm 0.3376$	$0.7324 \pm 0.2403$	0.209	
Nitrate	$16.3928 \pm 20.0067$	$11.2901 \pm 4.7658$	0.673	
ТОМ	$0.6903 \pm 0.2331$	$0.5057 \pm 0.2999$	0.242	
ТСНО	$218.1537 \pm 74.9417$	$169.7333 \pm 56.3371$	0.307	
TPRT	$164.335 \pm 34.02731$	$238.3967 \pm 129.5957$	0.046	
TLPD	$89.1331 \pm 29.7208$	$67.2467 \pm 3.2223$	0.230	
LOM	$471.6219 \pm 88.1148$	$475.3767 \pm 104.5025$	0.948	
BPC	$234.6355 \pm 39.7196$	$235.1427 \pm 52.0138$	0.985	
PRT Nitrogen	$26.2936 \pm 5.4444$	$38.1435 \pm 20.7353$	0.046	
PRT : CHO	$0.8472 \pm 0.4012$	$1.6107 \pm 1.2636$	0.050	
LPD : CHO	$0.4516 \pm 0.1954$	$0.4253 \pm 0.1317$	0.828	
LOM : TOM	$0.0780 \pm 0.0351$	$0.1626 \pm 0.1740$	0.065	

has a control over the amount of organic matter. Dissolved inorganic nutrients are highly bioavailable; they are incorporated into benthic and pelagic food webs within hours to days and thereafter are found as particulate organic matter<sup>58</sup>. No other significant correlations were observed (Table 2).

Comparison of mean values of the analyzed parameters and results by one-way ANOVA (Table 3) indicated that the sedimentary parameters like total proteins, protein nitrogen and PRT: CHO ratios between Kavaratti and Pitti (p<0.05) were statistically significant. Hence, statistical analysis also supported that there is considerable difference in these parameters between the two islands.

### Conclusion

Quantity and quality of sediment organic matter are largely dependent upon several factors including origin, composition and biochemical transformations that occur on organic particles during their descent to the water column. Organic matter has a significant role in understanding the carbon balance of the coral reef ecosystem.

Lakshadweep, an area of biogeochemically significance due to isolation from the major coastline,

possesses beautiful coral reefs and atolls and is well known as one of the biodiversity hot spots of the country. The present study is an attempt to compare the spatial distribution of biochemical composition in the sedimentary environments of an inhabited island, Kavaratti and an uninhabited island, Pitti belonging to Lakshadweep archipelago.

Compared to Pitti, sedimentary organic matter was slightly higher in Kavaratti, which is enclosed by a lagoon with plenty of coral reefs. But, there was no difference in the labile fraction of the organic matter. However, the percentage ratio of the labile to total organic matter indicated that most of the deposited organic matter is refractory in both environments. The higher PRT:CHO ratios in Pitti sediments compared to that of Kavaratti indicated that in Pitti, there is low dead organic matter accumulation, as it is uninhabited and also probably due to the strong hydrodynamic condition prevailing in the island. On the contrary, the low hydrodynamic condition in Kavaratti, as it is enclosed with a lagoon, favours the accumulation of sedimentary organic matter. This was well clear from the lower PRT:CHO ratios (<1) in Kavaratti sediments which indicated the presence of aged or less degradable

organic matter ie., terrestrial input. The lower LPD:CHO ratios estimated for sediments in both islands indicated low quality of labile organic matter to support benthic fauna. Statistical analysis by one-way ANOVA also supported the fact that there is significant difference in the total protein concentration and protein/carbohydrate ratio between Kavaratti and Pitti.

Among the inorganic nutrients, phosphate showed higher concentration in Pitti. Pitti is a bird sanctuary and the excreta of these birds might be an important source of inorganic phosphate. Pearson correlation analysis showed that significant positive correlations were observed between total organic matter and inorganic nutrients. This showed that nutrient concentration has a control over the amount of organic matter.

Biochemical composition was useful in the assessment of the quality and quantity of sedimentary organic matter and can provide a clear insight into the biogeochemical characterization of the sedimentary environments. Thus, it can be used to gather information on the origin and parameters controlling the diagenetic fate of organic matter. Information about processes controlling the delivery of organic matter to coastal environments and how the signatures of these inputs are reflected in newly deposited sediments is important to our understanding of global biogeochemical cycles.

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