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Distribution of amino acids in sediments of a mangrove ecosystem, west coast of India

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Abstract

The seasonal variability of free and protein bound amino acids (AAs) in the sediments of mangrove ecosystem, west coast of India were studied. AAs exhibited significant variability with depths in the sediments of two mangrove ecosystems, Mangalavanam and Vypeen, situated on the west coast of India. Of the ten AAs detected, serine (Ser) was the most abundant followed by threonine (Thr), glycine (Gly), aspartic acid (Asp), tyrosine (Tyr), glutamic acid (Glu) and alanine (Ala). The trend in AA relative abundance in the sediment and leaves exhibits a close similarity indicating a major influence of plants in the supply of these compounds to the sediment. The most common AAs at both stations are Asp, which is abundant in sediments with a large organic inputs followed by Glu, which is abundant in phytoplankton and marine bacteria. Ser, Thr and Gly, which constitute diatom cell walls, were also found in significant concentration. The changes in relative abundance of various AAs with depth indicate significant seasonal variability. This may be due to the selective microbial utilization of these AAs at different depths. Principal component analysis (PCA) revealed that the first principal component, which is the degradative index (PC_I) has ca. 84 % of the variance at Mangalavanam and

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ca. 92 % at Vypeen, suggesting that the concentration of individual AAs is more or less under the influence of a single process, i.e. microbial activity.

Keywords: Amino acids; Vertical distribution; Organic matter; Sediments; Mangroves; Cochin estuary.

1. Introduction

Amino acids (AAs), the structural components of proteins, represent one of the labile classes of organic matter (OM) in marine sediments. Proteins, peptides and free AAs account for 30–40% of the total nitrogen and 10–15% of the total organic carbon in marine surface sediments[1,2]. Sediments contain a mixture of proteins and amino acid degradation products[3] and mangrove sediments can be considered AA as large reservoirs. They most likely form the principal source of nitrogen for benthic heterotrophs[4, 5, 6]. Contributors of AAs to the mangrove systems are mangrove leaves, land run-off and in situ production. They exist in sediments in several forms, such as free AAs in the sediment micropores, as peptides or proteins bound to clay minerals, and as mucoproteins or muramic acid. They are readily decomposed by microorganisms and have only an ephemeral existence in soil. Their decomposition depends mainly on the type and concentration of the microbes responsible for the decomposition of particular compounds in the system. As a result, certain compounds will be completely removed from the system and others will be present in high concentration i.e. in general, different compounds will be present with a different composition irrespective of origin. The presence of an AA is affected by the decomposition of proteins, brought by bacteria, so decomposition affects the presence of a particular compound in a system.

AAs derived from different sources are useful indicators of OM diagenesis. Its decomposition provides an important pathway in the recycling of organic carbon and nitrogen[7]. A major process in the early stage of protein digenesis is the degradation to free AAs via various polypeptides as well as condensation with other organic compounds to form humic substances. Though peptides are believed to be important intermediates in the degradation process, their presence in sediments has generally been suggested generally from the analyses of AAs released by acid hydrolysis. The individual AAs and their abundances relative to each others are significant indicators of depositional environment and hence, offers more insight into the processes of diagenesis.

Normally, many of the essential AAs will not be available within the body of the aquatic organisms or in the system in which they live. Fertility of the system depends on the availability of such organic compounds and many AAs come under this category. Mangroves are considered as one of the major nurseries of aquatic life. In order to assess survival conditions of organisms in mangroves, it is important to understand stability of AAs in the sediments. The down-core variation provides the information on the extent of organic matter diagenesis in these sediments and to identify their sources. In the present study, the availability of hydrolysable amino acids in pore water or water is not considered as the storage of these compounds in an aquatic system occurs particularly in the sediment. In a complex environmental system, the distribution and actual concentration of a matter will be dependent on a large number of processes. Such a complex system can be analysed by considering the effective contribution of each process for a particular parameter. This differentiation and identification of the significance of the processes are done by factor analysis using SPSS 7, version 2.4 (1995-1998 ACD systems Ltd) to obtain the specific character of the AAs. Factors, which have eigen values with % variance more than 1, are taken for further analysis and discussed.

2. Experimental

2.1. Study Area

In this study, two different mangrove ecosystems (Mangalavanam and Vypeen) near Cochin estuary (Lat 10°27′ N and Long. 76°15′ E) in the west coast of India were chosen (Fig.1)

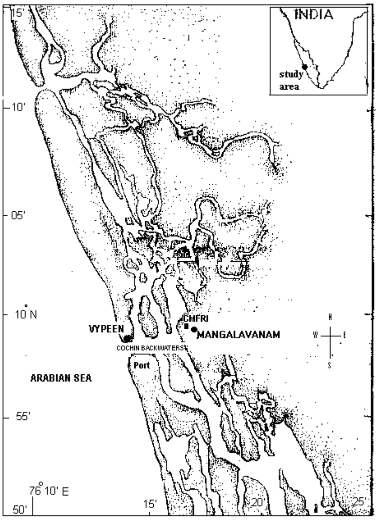

Fig. 1. Study site showing the sample location in the Cochin estuary

Mangalavanam (total area ca. 3.44 hectares), adjacent to the Central Marine Fisheries Research Institute (CMFRI), is connected to Cochin estuary by means of a canal. The tidal effect is limited to the discharge through the canal only. Vypeen (total area ca. 101 hectares), is an island close to the bar mouth. It is the largest single stretch of mangroves found in Kerala, regularly inundated by a semi diurnal rhythm of Cochin barmouth. The main species of mangrove plants found at both stations are Avicennia *marina*, Acanthus *ilicifolius* and Rhizophora *mucronata*. There is not much distinct seasonal variations in temperature in these study sites, and temperature is more or less uniform throughout the year. However, highest temperatures tend to occur in the summer months of March to May. Both Mangalavanam and Vypeen experience high rainfall during monsoon season that starts by the end of May and continues until September. Comparatively lower temperature is observed during winter from December to February.

2.2. Sample Collection and Pre treatment

The core sediments were collected on April, August and December 2002 representing the three seasons – summer, monsoon and winter. Cores to a depth of 30 cm from both stations were taken by pushing long PVC tubes into the sediment. These cores were cut with a plastic knife into six pieces as, from the surface (0-5), sub surface (5-10), 10-15, 15-20, 20-25 and 25-30 cm depths. The cores were then air dried, powdered using a mortar and pestle and stored in plastic vials for further analysis. The leaves of the plants Avicennia *marina*, Acanthus *ilicifolius* and Rhizophora *mucronata* were also collected from several plants and trees in the same area (10-50 m apart), air dried, powdered and kept airtight in plastic containers. The plastic containers used for the storage of all the samples were soaked in 1: 1 nitric acid and washed thoroughly with water and finally rinsed with distilled water.

3. Analysis

Total hydrolysable amino acids (THAAs) analyses were carried out by the method adopted by 8. An air-dried sediment samples (ca. 20 mg) were weighed in clean pre-weighed small boiling tubes. Each tube was inserted in 10 ml screw-capped vials in which1 ml of a mixture of 7 mol/L HCl, 10% trifluroacetic acid and 0.1% phenol were added. After flushing for about 2 minutes with high purity N_2 the vials were tightly closed. Vapour hydrolysis was carried out at 156^{o}C for 23 minutes. After cooling, the vials were opened and the tubes taken out cooled and dried under a stream of nitrogen gas to remove any acid present. Fluorescent AAs derivatives were prepared by treating the hydrolysate with OPA reagent and these derivatives were then separated by reverse phase HPLC with detection of the individual amino acid peaks by flourimeter at excitation wavelength 340 nm and emission wavelength 452 nm. Solvent gradients were formed using acetate/borate buffer and methanol in the ration 60:40. Separations were then carried out on a Cosmosil C_{18} column 150 mm x 4.6 mm, internal diameter 5 micron particles size. Best separation of as much as 13 amino acids was obtained with a flow rate of 1 ml/minute. The identification of individual amino acids in the samples was determined by comparing the retention times of peaks in samples with those in standard solution. All glassware used in this procedure were cleaned by soaking in 10% HCl for at least 1hr and rinsed with warm tap water and again two times with milliQ water, dried in oven at 150^{o}C for 2 hrs

3. Results and discussion

Of the twenty-two naturally occurring AAs, which are reported to have significant concentration in the aquatic system, only ten were quantified upon acid hydrolysis. Various AAs detected in sediments of Mangalavanam and Vypeen were Asp, Glu, Ser, Thr, Gly, Ala, Tyr, Val, Phe and Trp. Although these ten different amino acids were detected, only the first seven were found in significant concentrations. The HPLC chromatograms obtained for amino acid standards, surface (0-5cm depth) sediment samples and Avicennia leaves of both stations are given in Fig. 2-6 respectively.

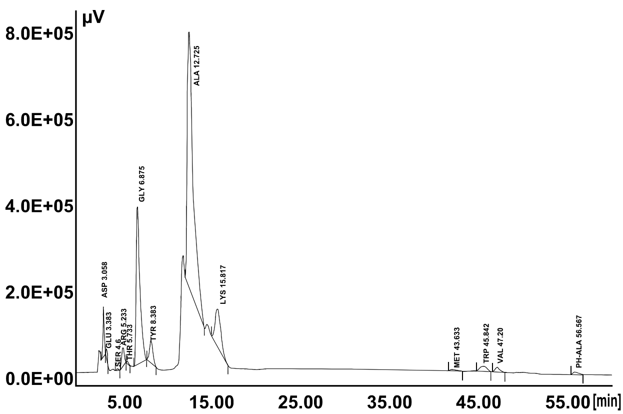

Fig. 2. Peaks for Amino acids Standards

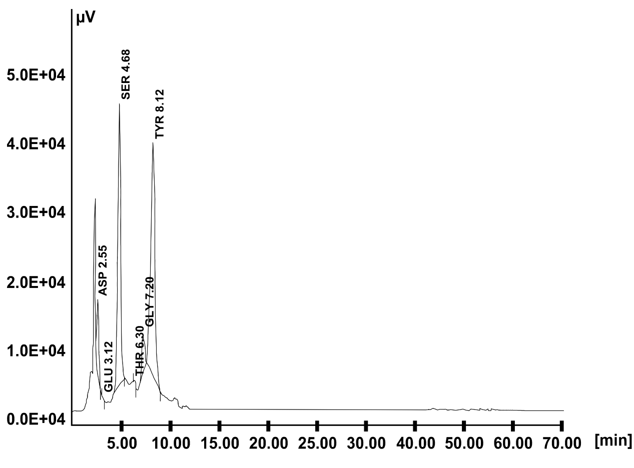

Fig. 3. Peaks of Amino acids in the sediment (0-5 cm depth) at Mangalavanam during monsoon season

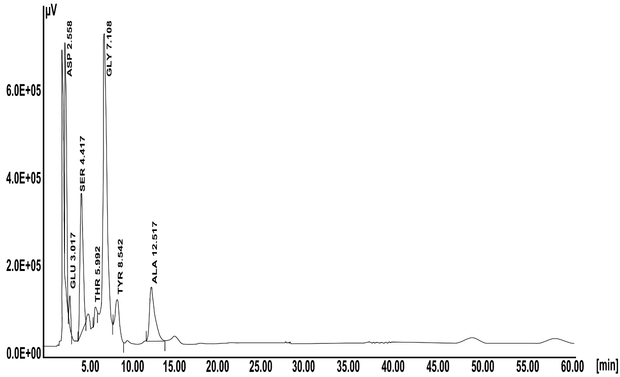

Fig. 4. Peaks of Amino acids in the sediment (0-5 cm depth) at Vypeen during monsoon season

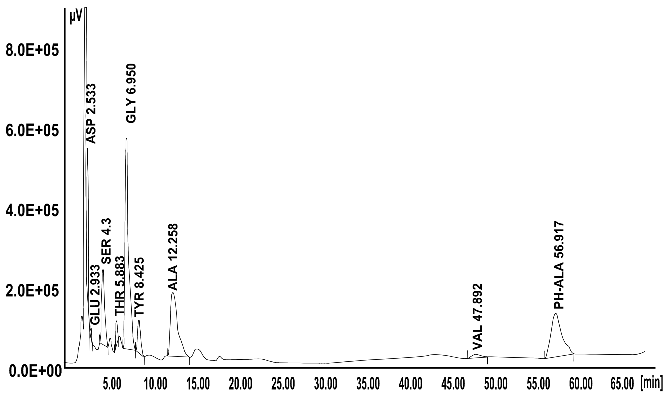

Fig. 5. Peaks of Amino acids obtained for the Avicennia plant species at Mangalavanam

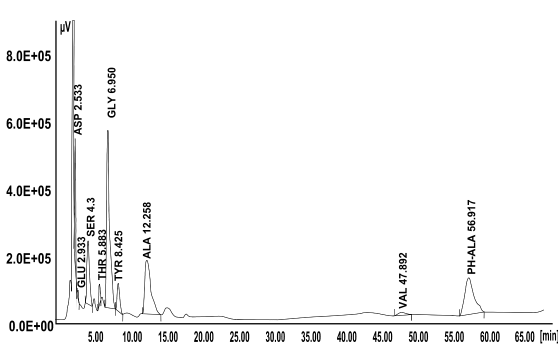

Fig. 6. Peaks of Amino acids obtained for the Avicennia plant species at Vypeen

The vertical distribution of various amino acids (μM) in sediment core at Mangalavanam and Vypeen are given in Fig. 7. The relative abundance (RA) of various AAs in the sediments and various plant leaves of Mangalavanam and Vypeen are presented (Tables 1-4).

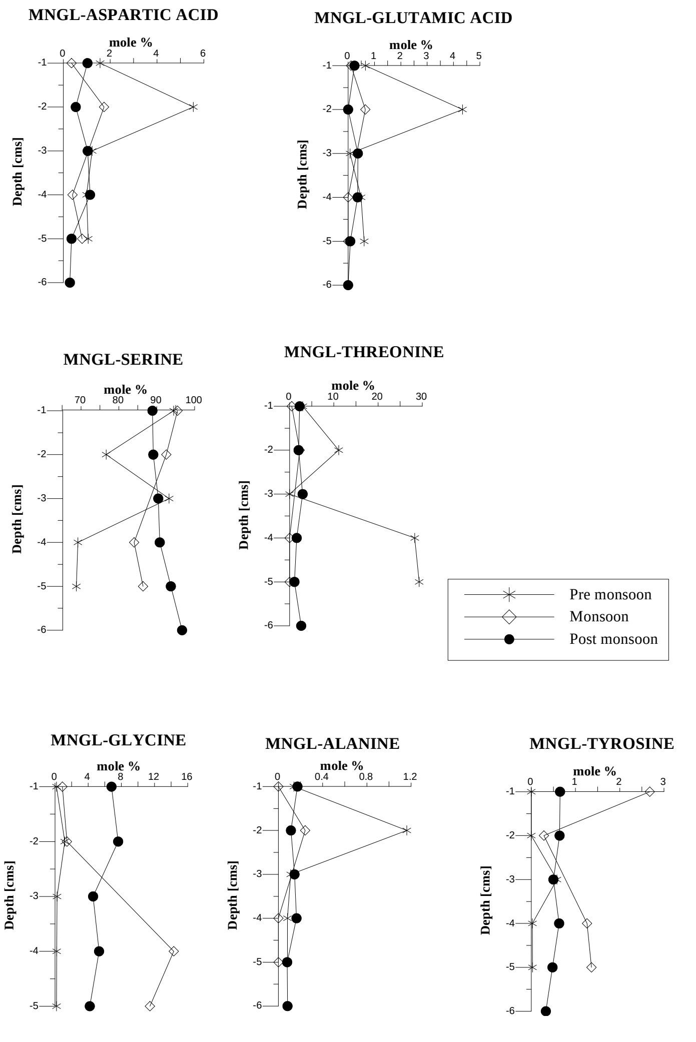

Fig.7. Distribution of amino acids (mole %) in the sediment core at Mangalavanam. .

$$\text{RA or mole \%} = \frac{\text{Concentration of individual amino acid x 100}}{\text{Concentration of total amino acids}}$$

Table 1. Relative Abundance (RA) or Mole % of amino acids in the sediment core at Mangalavanam

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Pre monsoon	0-5	1.570	0.657	94.47	2.984	0.176	0.000	0.140
	5-10	5.550	4.334	76.46	11.10	1.174	0.000	1.161
	10-15	1.230	0.074	93.27	0.000	0.241	0.579	0.111
	15-20	0.992	0.482	69.17	27.99	0.205	0.025	0.081
	20-25	1.063	0.607	68.75	29.29	0.184	0.027	0.082
Monsoon	0-5	0.346	0.113	95.48	0.499	0.088	2.683	0.000
	5-10	1.741	0.654	92.54	2.267	1.436	0.285	0.242
	15-20	0.393	0.000	84.04	0.000	14.32	1.257	0.000
	20-25	0.803	0.000	86.39	0.000	11.44	1.364	0.000
Post monsoon	0-5	1.026	0.236	88.86	2.256	6.806	0.648	0.172
	5-10	0.527	0.000	89.08	2.031	7.611	0.643	0.113
	10-15	1.044	0.367	90.40	2.955	4.593	0.496	0.146
	15-20	1.138	0.358	90.79	1.606	5.311	0.631	0.164
	20-25	0.348	0.078	93.72	1.105	4.187	0.479	0.079
	25-30	0.278	0.000	96.69	2.616	0.000	0.332	0.082

Table 2. Relative Abundance (RA) or Mole % of amino acids in the sediment core at Vypeen.

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Pre monsoon	0-5	1.352	0.000	88.29	7.823	2.068	0.302	0.158
	5-10	1.989	0.665	88.68	6.638	1.781	0.000	0.251
	10-15	0.489	0.000	89.66	6.100	3.629	0.000	0.124
	15-20	0.461	0.000	93.79	3.164	2.404	0.000	0.179
	20-25	0.949	0.672	86.11	1.696	8.278	2.190	0.109
	25-30	1.433	1.188	92.58	0.000	4.021	0.632	0.146
Monsoon	0-5	1.980	2.194	89.34	4.076	1.602	0.644	0.160
	5-10	0.550	0.319	90.39	0.000	6.607	1.955	0.172
	10-15	0.321	0.367	62.85	0.000	11.29	0.000	0.157
	15-20	1.681	1.572	90.37	2.849	1.818	1.167	0.171
	20-25	1.405	1.424	94.45	1.032	0.095	1.444	0.152

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Post monsoon	0-5	0.954	1.107	71.50	2.109	1.422	0.966	0.104
	5-10	0.819	0.000	41.81	0.000	25.96	19.14	0.109
	10-15	0.985	0.838	86.56	2.694	3.162	2.373	0.153
	15-20	0.950	1.139	92.45	3.626	1.101	0.707	0.029
	20-25	0.340	0.289	90.75	0.000	8.449	0.126	0.044
	25-30	1.932	0.000	44.43	0.000	52.39	0.993	0.250

Table 3. Relative Abundance (RA) or Mole % of amino acids in Plant leaves at Mangalavanam.

Plants	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Acanthus	1.118	0.172	87.65	10.47	0.139	0.044	0.339
Avicennia	1.808	0.879	66.83	9.669	0.129	0.376	0.255
Rhizophora	2.375	0.539	83.48	3.090	0.041	0.707	0.396

Table 4. Relative Abundance (RA) or Mole % of amino acids in Plant leaves at Vypeen.

Plants	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Acanthus	1.518	0.849	85.31	10.79	0.144	0.858	0.406
Avicennia	4.428	-	74.77	9.425	0.126	0.827	0.194
Rhizophora	1.386	3.725	72.21	16.84	0.224	1.152	0.397

At both stations AAs differed in their relative abundance. Ser, Thr, Gly and Ala were aliphatic neutral AAs, whereas, Asp and Glu were aliphatic acidic AAs. Ser was the most abundant AA, followed by Thr, Gly, Asp, Tyr, Glu and Ala. Of the two acidic AAs, Asp and Glu, Asp was found to be relatively more abundant than Glu at both stations. Contributors of AAs to the mangrove systems are leaves, land run-off and in situ production. The trend of relative abundance of AAs in sediment and leaves exhibits close similarity indicating a major influence of plants in the supply of these compounds to sediment. Seasonal vertical distribution of AAs (µM) in the sediment core at Mangalavanam and Vypeen is presented (Table 5-6).

Table 5. Seasonal vertical distribution amino acids (µM) in the sediment core at Mangalavanam.

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Pre monsoon	0-5	0.525	0.220	31.57	0.997	0.059	0.000	0.047
	5-10	0.068	0.053	0.937	0.136	0.014	0.000	0.014
	10-15	0.145	0.009	10.99	0.000	0.028	0.068	0.013
	15-20	0.361	0.175	25.18	10.19	0.075	0.009	0.029
	20-25	0.258	0.147	16.67	7.100	0.045	0.007	0.019
	25-30	1.556	0.658	0.000	2.511	1.809	0.319	0.171
Monsoon	0-5	0.022	0.007	6.075	0.032	0.056	0.171	0.000
	5-10	0.264	0.099	14.02	0.344	0.218	0.043	0.037
	15-20	0.027	0.000	5.698	0.000	0.971	0.085	0.000
	20-25	0.062	0.000	6.627	0.000	0.878	0.105	0.000
	25-30	0.007	0.013	0.000	0.000	0.049	0.000	0.000
Post monsoon	0-5	0.191	0.044	16.57	0.421	1.269	0.121	0.032
	5-10	0.059	0.000	9.937	0.227	0.849	0.072	0.013
	10-15	0.160	0.056	13.84	0.452	0.703	0.076	0.022
	15-20	0.110	0.035	8.791	0.156	0.514	0.061	0.016
	20-25	0.038	0.009	10.31	0.122	0.461	0.053	0.009
	25-30	0.034	0.000	11.93	0.323	0.000	0.041	0.010

Table 6. Seasonal vertical distribution amino acids (µM) in the sediment core at Vypeen.

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Pre monsoon	0-5	0.396	0.000	25.85	2.290	0.606	0.088	0.046
	5-10	1.252	0.419	55.84	4.180	1.121	0.000	0.158
	10-15	0.065	0.000	11.93	0.812	0.483	0.000	0.017
	15-20	0.112	0.000	22.88	0.772	0.586	0.000	0.044
	20-25	0.072	0.051	6.522	0.128	0.627	0.166	0.008
	25-30	0.580	0.480	37.45	0.000	1.626	0.256	0.059
Monsoon	0-5	1.193	1.322	53.82	2.456	0.965	0.388	0.097
	5-10	0.101	0.058	16.53	0.000	1.208	0.357	0.031
	10-15	0.029	0.033	5.733	0.000	1.031	0.000	0.014
	15-20	0.613	0.574	32.98	1.040	0.663	0.426	0.062
	20-25	0.419	0.425	28.16	0.308	0.028	0.431	0.045

Season	Depth (cms)	Asp	Glu	Ser	Thr	Gly	Tyr	Ala
Post monsoon	0-5	0.419	0.487	31.43	0.927	0.625	0.425	0.046
	5-10	0.017	0.000	0.881	0.000	0.547	0.404	0.002
	10-15	0.197	0.167	17.28	0.538	0.631	0.474	0.031
	15-20	0.550	0.660	53.56	2.101	0.638	0.410	0.000
	20-25	0.022	0.018	5.771	0.000	0.537	0.008	0.003
	25-30	0.018	0.000	0.403	0.000	0.475	0.009	0.002

At Mangalavanam, the relative abundance of both acidic AAs, Asp and Glu was found to be the highest during pre monsoon season at the sub surface (5-10cm) (5.55 mole % and 4.33 mole % respectively). The highest mole % of hydroxy AAs, Ser and Thr were found at deeper sections of the sediment core. Ser was found to be a maximum of 96.7% at 25-30 cm depth during post monsoon season and Thr, 29.29% at 20-25 cm depth of the core during pre monsoon season. The maximum abundance of neutral AA Gly was observed at 15-20 cm depth (14.32 mole %) during monsoon season and Ala at the subsurface (5-10 cm) during pre monsoon season (1.16 mole %).

At Vypeen the highest mole % of Asp (1.99) was observed at 5-10cm depth during pre monsoon and Glu (2.194) at surface during monsoon season. The highest mole % of Ser (94.5) was at 20-25 cm during monsoon season and Thr (7.8) at the surface during pre monsoon season. Gly was found to be the highest (52.4%) at 25-30 cm depth during post monsoon and Ala, highest mole % (~0.25 mole %) was observed at 5-10 cm and 25-30 cm depth during both pre monsoon and post monsoon seasons respectively.

Tyr, an aromatic neutral AA, was present very less in the deeper core sections and absent at the surface and sub surface depths at Mangalavanam, where the highest mole% (2.68) was seen at the surface during monsoon season. At Vypeen, the highest mole% was observed at the sub surface (19.14 mole %) during post monsoon season.

The behavior of AA concentrations at the two stations is different. At Mangalavanam, which is a closed system, during pre monsoon season there is very little chance for organic matter (OM) to get flushed away from the system. This suggests a very long residence time for mangrove detritus in anaerobic sediments. Sometimes due to less tidal inundation the sediment surface gets direct contact with atmospheric air leading to aerobic decomposition of OM along with the usual anaerobic decomposition. Tidal influence will be comparatively less during post monsoon season. But during monsoon, fresh water abundance in the system due to rainfall and high tidal inflow enable the flushing of OM from the system. Due to this, a reproducibility of the values of AA concentrations may not be expected at Mangalavanam. At Vypeen human intervention and aquatic life are more than that at Mangalavanam due to the semi open nature of the system and hence the reactivity here is governed by these factors. During all the seasons tidal flushing will be there at Vypeen since it is close to the sea and estuary.

The most commonly occurring acidic AAs in the present study were Asp and Glu. Asp was found more abundant than Glu in almost all depths at both stations. Glu is generally abundant in phytoplankton and marine bacteria[9] and also sediments receiving large inputs of OM were found to be rich in Asp[10]. Basic AAs, especially Lys, are more common in offshore sediments due to the more stability in such depositional environments [11]. There is absence of significant amount of basic AAs in the present study. Basic AAs and aromatic AAs containing sulphur are labile and easily lost in sediments during geochemical degradation of sedimentary OM.

Glu and Tyr are cell plasma compounds and they are considered relatively more labile than other AAs. In general, labile AAs undergo decomposition easily, whereas refractory AAs remain in the system. AAs are either non-reactive or degraded at slower rates. Burdige and Martens[1] reported that the changes in total AA concentrations with depth are due to utilization of labile AAs in microbially mediated reactions such as fermentation, sulphate reduction and methanogenesis. The variation in the concentration of individual AAs in the sediments of Mangalavanam and Vypeen may be due to their selective microbial utilization indicative of various biogeochemical activities at different depths.

Ser, Thr and Gly were the most abundant AAs at Mangalavanam and Vypeen. These AAs are enriched in the cell wall protein of the diatoms and hence considered to be selectively preserved by the protein-silica complex of diatom cell walls[12]. AAs concentrations found to be higher in reducing sedimentary environments[13] and generally stable and resistant to environmental degradation[1,14]. The abundance of these AAs in the two mangrove sediments in the present study can therefore be attributed to their greater stability. In order to evaluate quantitative similarities and differences in the dynamics of the individual AAs, a correlation matrix of amino acids was calculated using AA (mole %) data (Tables 7,8,9). At Mangalavanam, in all depths Asp, Glu and Ala showed significant positive correlation to one another (Table 8) implying that these group of AAs was subject as a whole to similar mechanisms of biogeochemical alteration in the system. Ser and Thr showed strong negative correlation (Table 8) suggesting their different diagenetic behavior.

Table 7. Coefficient of determination (R^2) for Amino acids (mole %) and Total Amino acids TAA in the sediment core at Mangalavanam (n=15) and Vypeen (n=17).

Amino acids	Mangalavanam		Vypeen	
	Mean	Std. Deviation	Mean	Std. Deviation
Asp	.0120	.0128	.0112	.0056
Glu	.0053	.0108	.0072	.0068
Ser	.8775	.0921	.8494	.1489
Thr	.0580	.0971	.0250	.0025
Gly	.0391	.0449	.0847	.1340
Tyr	.0063	.0070	.0210	.0514
Ala	.0017	.0028	.0015	.0006
TAA	1.560	1.068	2.812	2.159

Table 8. Pearson Correlation matrix of individual amino acids in terms of relative abundance (mole %) and Total Amino acids (TAA) in the sediment core at Mangalavanam.

	Asp	Glu	Ser	Thr	Gly	Tyr	Ala	TAA
Asp	1.000							
Glu	0.977**	1.000						
Ser	-0.328	-0.402	1.000					
Thr	0.196	0.268	-0.879**	1.000				
Gly	-0.263	-0.273	-0.009	-0.405	1.000			
Tyr	-0.403	-0.365	0.347	-0.468*	0.332	1.000		
Ala	0.971**	0.978**	-0.277	0.136	-0.234	-0.382	1.000	
TA	-0.184	-0.202	-0.338	0.603*	-0.396	-0.498	-0.295	1.000

**Correlation is significant at the 0.01 level * Correlation is significant at the 0.05 level.

Table 9. Pearson Correlation matrix of individual amino acids in terms of relative abundance (mole %) and Total Amino acids (TAA) in the sediment core at Vypeen (n=17).

	Asp	Glu	Ser	Thr	Gly	Tyr	Ala	TAA
Asp	1.000							
Glu	0.507*	1.000						
Ser	-0.197	0.430*	1.000					
Thr	0.261	0.008	0.350	1.000				
Gly	0.128	-0.463*	-0.943**	-0.474*	1.000			
Tyr	-0.074	-0.230	-0.643**	-0.301	0.403	1.000		
Ala	0.474*	-0.105	-0.275	0.082	0.325	-0.142	1.000	
TAA	0.549	0.668	0.508	0.524	-0.593	-0.333	0.017	1.000

**Correlation is significant at the 0.01 level. * Correlation is significant at the 0.05 level.

At Vypeen significant positive correlation observed between Asp and Glu (Table 9) suggesting similar diagenetic behaviour in between them (R^2= 0.507, p< 0.01, n=17), whereas, a negative correlation is observed between Gly and Ser (R^2= 0.943; p< 0.001; n=17) and between Tyr and Ser (R^2=0.643; p< 0.01, n=17), which are indicative of their different diagenetic behaviour. At Mangalavanam, Thr alone showed significant positive correlation with TAA (0.603, n=15, p< 0.01), but at Vypeen Asp, Glu, Ser and Thr showed significant positive correlation (R^2 =0.549, 0.668, 0.508, 0.524, n=17, p< 0.01) and Gly showed significant negative correlation (R^2= -0.593, n=17, p< 0.01) with TAA.

Sediment characteristics of both Mangalavanam and Vypeen mangroves cannot be compared with other reported observations like that in seawater, estuaries etc. The preliminary analysis of the reactivity of sediments (Nunn and Keil, 2004) earmarks the first few centimeters of the sediment as reactive zones and rest almost stable or inert. But in case of estuaries and restricted aquatic systems like mangroves, salt marshes etc it has been shown that sediment is reactive even until 30 cm depth.

The PCA result including eigenvalue and their contribution to the explained variance at Mangalavanam and Vypeen are given in Table 10 and 11respectively.

Table 10. % of variance for the initial eigen values of the first three components in PCA of amino acids (mole %) at two stations.

Components	Mangalavanam % of Variance	Vypeen % of Variance
1	83.59	91.85
2	13.96	6.27
3	2.20	1.69

Table 11. Results of Principal Component Analysis (PCA) based on relative abundance (mole %) of Amino acids in the sediment core at two stations (n=15).

Amino acids	Mean Value		Std. Deviation		Factor Coefficients					
					Mangalavanam (Mngl)			Vypeen (Vyp)		
	Mngl	Vyp	Mngl	Vyp	PC1	PC2	PC3	PC1	PC2	PC3
Asp	0.012	0.011	0.013	0.006	0.967	-0.138	-0.126	0.229	-0.030	0.462
Glu	0.005	0.007	0.011	0.007	0.961	-0.215	-0.127	-0.451	-0.098	-0.046
Ser	0.878	0.849	0.092	0.149	-0.221	0.966	-0.134	-0.888	-0.459	0.013
Thr	0.058	0.025	0.097	0.025	0.024	-0.948	-0.316	-0.314	-0.122	0.933
Gly	0.039	0.085	0.045	0.134	-0.136	0.095	0.985	0.972	0.170	-0.161
Tyr	0.006	0.021	0.007	0.051	-0.195	0.373	0.308	0.224	0.965	-0.127
Ala	0.002	0.002	0.003	0.001	0.966	-0.082	-0.102	0.413	-0.202	0.234

Rotation Method: Varimax with Kaiser Normalization.

When eigen values greater than 1 are considered, we get three factors for each station. It is evident from the PCA of both stations, that the first component, which is the degradative index (PC_I) has ~84 % of variance at Mangalavanam and ~92 % of variance at

Vypeen. The second component (PC_{II} or adsorption component) has a significant contribution of about 14 % at Mangalavanam and ~6.5 % at Vypeen. AAs obtained in the microanalysis include those from the hydrolysis of protein and free amino acids (FAA) available in the system. FAA concentration is more or less governed by microbial action, but not in protein. The concentration of different AAs in protein depends on

1. Decomposition patterns of protein itself (i.e. which bond is broken and which AAs are released or which AA is totally degraded).

2. Depends on protein source.

3. AAs adsorbed to the sediment (the binding capacity of each AA depend on the sediment type and system character, i.e., each AA have different binding capacity in different sediments). The study showed that the seasonal variability is primarily governed by microbial activity[17]. There will be supplementary factors like adsorption, lateral addition etc. but that has only very low significance because the major part of adsorbed AAs will be forming a part of free AAs. Considering the degradation index, from the factor coefficient values 0.967, 0.961 and 0.966, it is evident that concentrations of AAs like Asp, Glu and Ala are governed by microbial processes at Mangalavanam, since they come in the first factor. At Vypeen, mainly Gly (factor coefficient, 0.972) and Ala (factor coefficient, 0.413) have significance in the first component. The comparatively higher positive values of their factor coefficients indicate their higher or positive contribution towards microbial degradation than the other amino acids. At Vypeen, Ser and Glu (factor coefficient, -0.888 and -0.451 respectively) showed a significant negative factor coefficient value, which is indicative of less microbial degradation.

4. Conclusion

This study showed that Ser, Asp, Glu, Gly, Thr, Ala, Tyr, Val, Phe and Trp are the dominant AAs found in sediments of mangrove ecosystem (Mangalavanam and Vypeen), situated on the west coast of India. Although AAs did not vary in their composition and relative abundance at both stations, it revealed that there is a significant seasonal variability with depths. The trend in AA relative abundance in the sediment and leaves exhibits a close similarity indicating a major influence of plants in the supply of these compounds to the sediment. The most common AAs at both stations are Asp, which is abundant in sediments with a large organic inputs followed by Glu, which is abundant in phytoplankton and marine bacteria. Ser, Thr and Gly, which constitute diatom cell walls, were also found in significant concentration. The changes in relative abundance of various AAs with depth indicated a significant seasonal variability due to the selective microbial utilization at different depths. Principal component analysis (PCA) revealed that the first principal component, which is the degradative index (PC_I) has ca. 84 % of the variance at Mangalavanam and ca. 92 % at Vypeen, suggesting that the concentration of individual AAs is more or less under the influence of a single process, i.e. microbial activity.

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