

## Dissolved, particulate and sedimentary humic acids in the mangroves and estuarine ecosystem of Goa, west coast of India

Sugandha Sardessai

National Institute of Oceanography, Dona Paula, Goa-403004, India

Received 3 February 1992, revised 12 October 1992

Highest concentration of humic acids in all the three forms (dissolved, particulate and sedimentary) was found in the monsoon (June-Sept.) when the salinity was minimum while the lowest concentration was observed in the premonsoon (Feb-May) when the salinity was maximum. Sedimentary humic acids (SHA) level was relatively higher than the dissolved (DHA) and the particulate (PHA) humic acids except in the monsoon when the proportion of PHA exceeded than of SHA. The percentage of organic matter associated with humic acids in the sediments was maximum in the monsoon and minimum in the premonsoon season which may be attributed to the decomposition of the litter from the mangrove swamps as well as to the fresh water inflow from the upstream region. A positive correlation ( $r = .736$ ) is observed between organic carbon and humic acids in this mangrove ecosystem. Among the three stations, the one with a very thick population of mangroves was found to be the most productive with respect to humic acids.

Humic acids play a significant role in the biological cycle in the marine environment. Its importance in complexing the toxic heavy metals and in recycling the essential trace metals required for the growth of phytoplakton has been well realised<sup>1-4</sup>. Mangroves are one of the most productive natural ecosystems and are important part of the coastal and estuarine ecosystem. They play a major role towards the contribution of organic matter to the estuarine ecosystem in the form of litter which is converted into detritus by microbial degradation. However, the information on the humic acids fraction of the organic matter is scarce in this ecosystem. Seasonal variations of these materials as well as the relative proportions of dissolved, particulate and sedimentary fractions have not been studied earlier. The present paper reports seasonal variations and the relative fractions of the different forms of humic acids in this organically rich and productive environment as well as the adjoining estuarine system of Goa.

### Materials and Methods

Mandovi and Zuari are the largest tide dominated estuarine systems of Goa and they interact through the Cumbarjua canal (Fig. 1). The quantity of fresh water discharge during pre and post monsoon periods is negligible in both the river systems and therefore their flow during these seasons is regulated by semi-diurnal tides having a maximum range of 2.3 km. Maximum distance of penetration of water

( $\sim 0.09 \times 10^{-3}$  salinity) inland is about 65-70 km away from the mouth during premonsoon and following the onset of monsoon it gets reduced to a minimum of about 20 km.

The major mangrove species of Chorao island (st 1) are *Rhizophora apiculata*, *R. mucronata*, *Sonneratia alba*, *Kandellia candel*, *Avicennia marina*, *A. officinalis*, *Brugaria gymnorhiza* and *B. parviflora*. The ground flora consists of *A. officinalis* mixed with pneumatophores as well as seedlings of other mangroves. *Exocacteria agallocha* of about 1 to 2 m height forms the borderline of the mangrove zone, especially along the bunds. The mangrove species of Banastarim (st 2) are *R. mucronata*, *E. agallocha*, *A. officinalis* and *A. marina*, whereas the Borim (st 3)

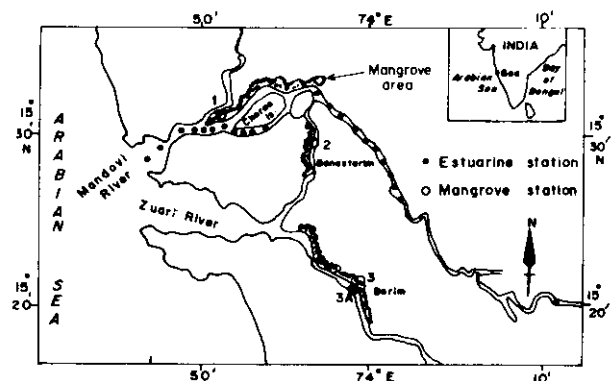


Fig. 1—Map showing station positions

mangrove swamps consists mainly of *R. mucronata* and *E. agallocha* species.

Surface water and sediment samples were collected monthly during low tides from July 1989 to July 1990. Water sample were collected in plastic bottles and sediment sample (10 cm deep) were collected in precleaned plastic bags and kept frozen in the laboratory until analysis. Surface water samples were also collected once in each season, in the Mandovi estuary at different stations (Fig. 1) from sea end to the fresh water end of the estuary representing the estuarine conditions for the mangrove swamps studied.

Water samples were analysed for the dissolved (DHA) and particulate (PHA) humic acids following the method of Martin and Pierce<sup>5</sup> and modified by Hair & Basset<sup>6</sup>. Sedimentary humic acids (SHA) were quantified by the method described in Shanmukhappa<sup>7</sup>. Organic carbon was estimated by the method of El-Wakeel & Riley<sup>8</sup> and salinity estimations were made by Mohr-Knudsen titrimetric method<sup>9</sup>.

## Results and Discussion

Seasonal variations of PHA and SHA along with variations in salinity at the 3 stations are shown in Fig. 2. DHA concentration was below the detection limit ( $< 0.5$  ppm) almost throughout the year except in July 1990, the maximum concentration being 0.8 ppm. PHA and SHA values showed distinct seasonal variations and were also related to salinity levels in the region. Higher concentrations of humic acids (PHA and SHA) were found in the monsoons (July-Sept. 89 and June-July 90) when the salinity was minimum while lower concentrations were observed in premonsoon (Feb.-May) when the salinity was maximum. The levels of PHA and SHA during the monsoon of 1989 were relatively lower than the monsoon (data for June, July only) of 1990. Further, the concentrations of these forms of HA were higher in May 1990 (premonsoon) as compared to the other premonsoon months. This may be due to the fact that in 1990 the onset of monsoon was in early May and was in full swing during June and July compared to the monsoon of 1989. This is also evident from the decrease in the salinity during May at all the three stations.

In general, SHA levels were relatively higher than the PHA except at st 3 in the monsoon when the PHA fraction exceeded that of SHA and at sts 1 and 2 PHA exceeded SHA in the monsoon 1990. Mangroves are known to harbour a pool of organic matter which is governed by tidal action, fresh water inflow, litter fall and the rate of primary production<sup>10</sup>. During the

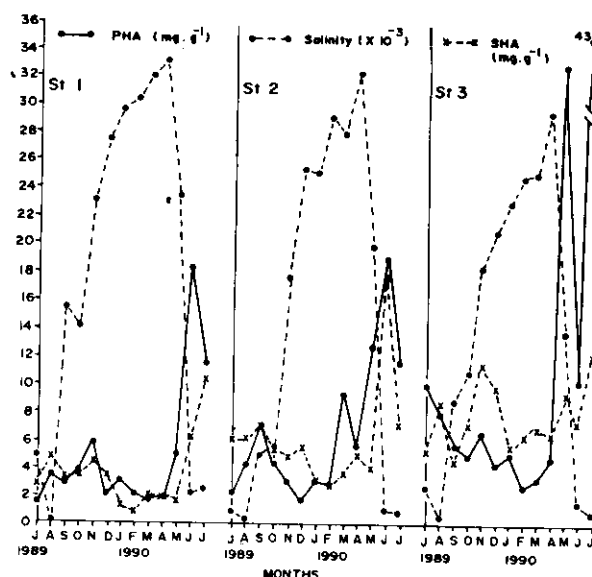


Fig. 2—Monthly variation of PHA, SHA and salinity at station 1-3

monsoon, terrestrial runoff contributes high levels of particulate matter with organic and inorganic constituents to mangrove swamps and surrounding waters. The export of organic matter due to tidal action from the mangrove environment is also very significant<sup>11-13</sup>. The increase or decrease of PHA level is intricately associated with the variation in the intensity of monsoonal rainfall and the resultant influx of water and transport of particles. Furthermore, the occasional resuspension of sedimentary particles during the monsoon also plays a significant role in the increase of PHA concentration in the mangrove ecosystem. These facts are evident from the observations made at sts. 3 and 3A in the mangrove and adjacent estuarine ecosystem at Borim.

Table 1 shows the variations of particulate matter (PM) and PHA of water and the PHA concentration of particulate matter at st 3 (mangrove area) and st 3A (adjacent estuarine ecosystem). Concentration of PM varied from one month to another as well from the monsoon of 1989 to the monsoon of 1990. The PM and the PHA concentration were higher at st 3 than at st 3A during July' 89, June and July' 90, whereas they were lower in August and Sept' 89 (monsoon months) which indicate that there is an occasional resuspension of sedimentary particles from the mangrove sediments which is rich in humic acids. PM of the mangrove area (st 3) is richer in PHA than the estuarine water particulate matter (st 3A) during July, August and Sept. 1989 whereas the same shows a decrease compared to the river water PHA in June and July 1990. These observations suggest that the

Table 1—Particulate matter(PM), particulate humic acid(PHA) and PHA of PM at sts 3 and 3A

Month	Station 3			Station 3A		
	PM (g.l <sup>-1</sup> )	PHA (mg.l <sup>-1</sup> )	PHA (mg.g <sup>-1</sup> of PM)	PM (g.l <sup>-1</sup> )	PHA (mg.l <sup>-1</sup> )	PHA (mg.g <sup>-1</sup> of PM)
July' 89	0.1754	1.76	10.0	0.1178	0.60	5.1
Aug.' 89	0.0470	0.37	7.9	0.1340	0.49	3.7
Sept.' 89	0.1172	0.67	5.7	1.0460	3.22	3.0
June' 90	0.3100	3.24	10.4	0.0208	0.66	31.5
July' 90	0.0390	1.66	42.7	0.0106	0.63	59.4

decomposed mangrove litter plays a dominant role in the supply of HA to the particulate matter whereas in June and July 90 the increase in the concentration of PHA in the mangroves (st 3) seems to be mainly due to the influx of fresh water rich in PHA.

Twilley *et al.*<sup>14</sup> found that average litter production in riverine mangroves is higher than that of fringe mangroves in southwest Florida. The litter fall is highest in the premonsoon (av 1934.5 g.m<sup>-2</sup>) and lowest in the monsoon (av 1409 g.m<sup>-2</sup>) for the 4 major mangrove species at Choroa island<sup>15</sup>. The mangrove litter undergoes degradation by bacteria and fungi. Poutanen and Morris<sup>16</sup> believe that the degradation of planktonic debris is a matter of weeks or months after deposition. Since the degradation of mangrove litter takes place on a similar time scale<sup>15</sup> it can be concluded that the litter fall mainly contributes to the high concentration of organic matter and humic acids observed in the monsoon.

A comparison of the PHA and SHA concentration of humic acids at the three stations (Fig. 2) depicts that in general, st 3 has a high concentration of humic acids as compared to sts 1 and 2. Station 3 is characterised by a thick population of mangroves and the area has small ponds. Besides, the area is cut off from the adjoining estuary during low tide which also helps in the retention of organic matter. Station 2 receives a part of its supply of organic matter from the fresh water which is evident from the low salinity at this station relative to st 1. Station 1 is dominated by salt water for a greater part of the year and although the water column is influenced by mangrove community the area has free excess to the estuary even during low tide.

The organic carbon in the sediments ranged from 1.03 to 2.75 % at st 1, from 1.78 to 3.12 at st 2 and from 2.46 to 5.41 % at st 3. Table 2 shows the percentage of humic acids in the sediments and the

Table 2—Percentage of humic acids and the organic matter associated with humics in the sediments of mangrove area

Season	% of humic acids			% of organic matter associated with humics		
	St 1	St 2	St 3	St 1	St 2	St 3
1989 Monsoon (July-Sept.)	0.36	0.64	0.60	9.5	13.8	10.6
Postmonsoon (Oct.-Jan)	0.32	0.46	0.84	8.7	9.3	10.0
Premonsoon (Feb.-May)	0.16	0.38	0.74	6.0	7.6	11.1
1990 Monsoon (June-July)	0.83	1.24	0.98	29.8	21.0	18.8

percentage of organic matter associated with humics during different seasons. It can be observed that the percentage of humic acids is in general higher in the monsoon and lower in the premonsoon season except at st 3 which shows lowest concentration in the monsoon of 89. The percentage of organic matter associated with humics also showed similar pattern of variation which supports the observation that the organic matter production of the mangrove swamps is high in the monsoon. It is pertinent to note here that st 3 has the maximum concentration of humic acids during different seasons except in the monsoon of 90 when st 2 shows the highest concentration of humic acids. The exceptions to the pattern of variations indicate the varying input of humic acids to the sediments from one month to another through different sources of humic material.

The variation of SHA with organic carbon in the sediments is shown in Fig. 3. A fairly good positive

correlation is observed between organic carbon and SHA ( $r = .736$ ) in this mangrove ecosystem whereas the PHA does not show any significant correlation with salinity ( $r = .418$ ).

The seasonal variations in the dissolved and particulate HA were studied in the Mandovi estuary. The levels of DHA were very low ( $< 0.5$  ppm) and did not show any regular trend of variation. Showkovitz<sup>17</sup> has reported very low concentration of

DHA in the four rivers of Scotland and Sholkovitz *et al.*<sup>18</sup> have shown experimentally that the dissolved HA from the fresh water flocculates when it comes in contact with saline water and there is a maximum removal of HA between salinity  $0-15 \times 10^{-3}$ . In the present study a similar pattern of variation was observed in case of PHA. The plots of the variations of PHA with salinity in the three seasons (Fig. 4) show that in the monsoon and postmonsoon seasons the points do not lie on a straight line but follow smooth curves which are concave to the ideal mixing curve indicating that the PHA is removed or desorbed from the particulate suspended load. In the premonsoon PHA varied linearly with salinity ( $r = .904$ ). The maximum removal was found to take place between salinity  $0-5 \times 10^{-3}$  in the two seasons.

From the foregoing it can be concluded that the humic acids in the particulate matter as well as in the sediments of these mangrove swamps are contributed mainly by the decomposition of the litter and partly by the fresh water influx during the monsoons. The processes like resuspension and the variability in the transport of organic matter to the mangrove ecosystem during different seasons play a significant role in the humic acids concentration in the mangrove ecosystem. In the estuaries the dissolved humic acids form a negligible fraction of the humic acid component of organic matter whereas the

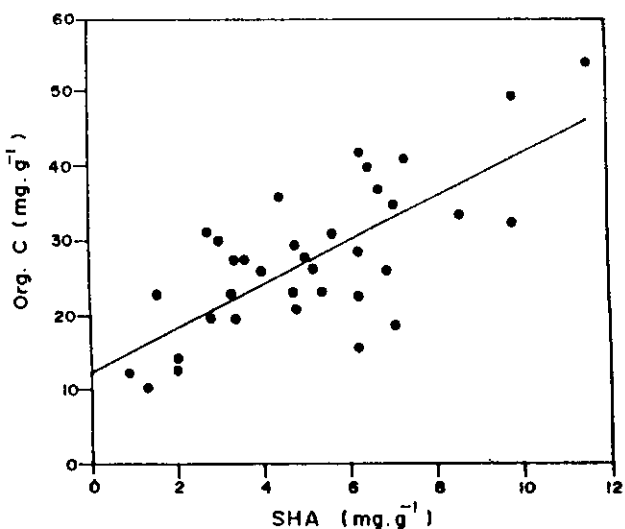


Fig. 3—Variation of organic carbon with SHA in the mangrove ecosystem

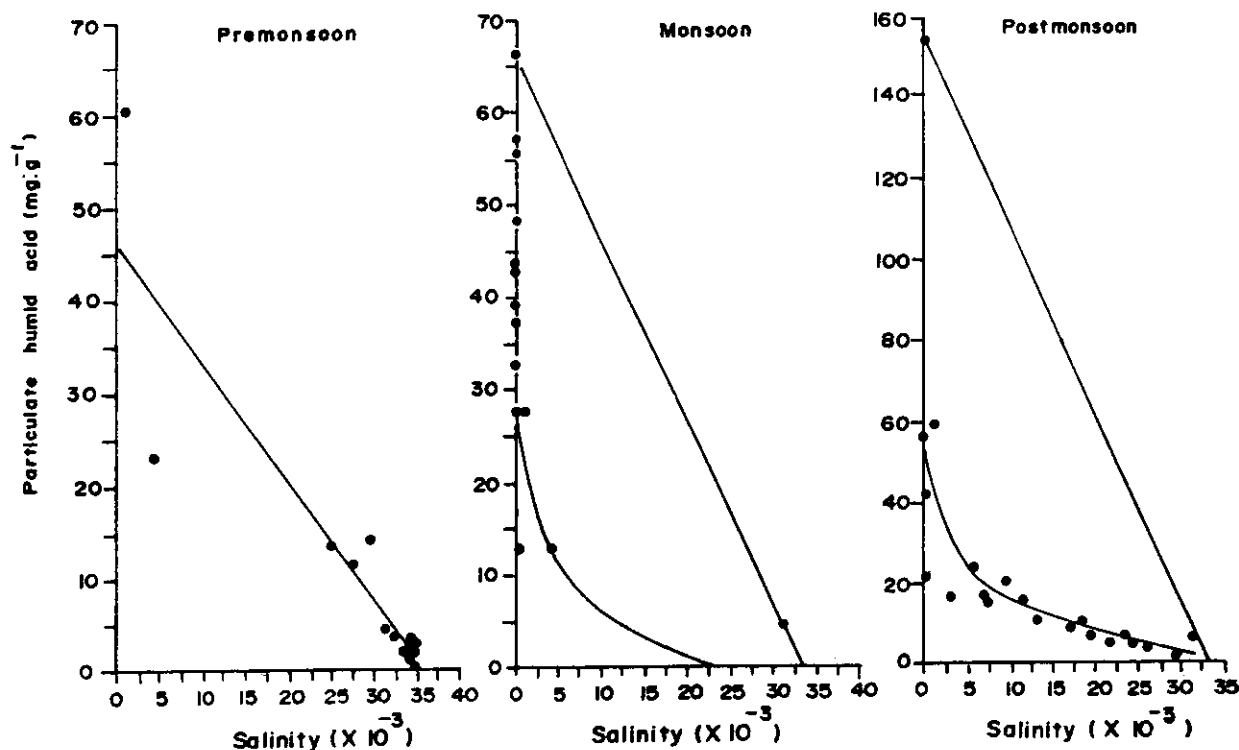


Fig. 4—Variation of PHA with salinity in the 3 seasons in the Mandovi estuary

particulate humic acid is the dominant fraction both in estuarine and fresh water zones and it is removed or desorbed when it mixes with saline water of low salinity range ( $0-5 \times 10^{-3}$ ). Since there is no increase in the DHA concentration with the decrease in the PHA concentration it is likely that the desorbed PHA might be added to the sediments of the estuary.

#### Acknowledgement

Author thanks Dr. B.N. Desai, Director for his keen interest in this work. The author also thanks Dr. R. Sen Gupta and Dr. A. Rajendran for reviewing the manuscript and making valuable suggestions. Thanks are also due to Dr. S.N. De Sousa for valuable suggestions during the course of this work and to Mr. H.S. Dalvi for technical help.

#### References

- 1 Manskaya S M & Drozodova T V, *Int series of monographs in earth science*, 28 (1968) 347.
- 2 Rashid M A, *Soil Sci*, 11 (1971) 298.
- 3 Rashid M A & Leonard J D, *Chem Geol*, 11 (1973) 89.
- 4 Rashid M A, *Chem Geol*, 13 (1974) 115.
- 5 Martin D F & Pierce R J Jr, *Environ Letts*, 1 (1971) 49.
- 6 Hair M E & Basset C R, *Estuar Coast Mar Sci*, 1 (1973) 107.
- 7 Shanmukhappa H, in "*Proceedings of international conference on environmental quality and ecosystem stability*, Vol 3, edited by Dubinsky Z & Y Steinberger, (Bar Ilan University Press, Ramat Gan, Israel) 1986, 211.
- 8 El- Wakeel S K & Riley J P, *J du Conseil Parm Inter Pour L'explor de la*, 22 (1956) 180.
- 9 Grasshoff K, *Methods of sea water analysis*, (Verlag-Chemie, New York) 1976, pp 317.
- 10 Jagtap T G, *Ecological studies in relation to the mangrove environment along the Goa coast, India*, Ph D thesis, Shivaji University, Kolhapur, India, 1985.
- 11 Golley F, Odum H T & Wilson R F, *Ecology*, 43 (1962) 9.
- 12 Odum W E & Heald E J, *Bull Mar Sci*, 22 (1972) 671.
- 13 Lugo A E & Snedaker S C, *The role of mangrove ecosystem: Properties of mangrove forest in south Florida*, Report No DI-DEEP, (University of Florida, Gainesville, USA) 1973-74, 34.
- 14 Twilley R R, Lugo A E & Patterson-Zucca C, *Ecology*, 67 (1986) 670.
- 15 Wafar S, *Ecology of the mangroves along the estuaries of Goa*, Ph D thesis, Karnataka University, Dharwar, India, 1987.
- 16 Poutanen E L & Morris R J, *Estuar Coast Shelf Sci*, 17 (1983) 189.
- 17 Sholkovitz E R, *Geochim Cosmochim Acta*, 40 (1976) 831.
- 18 Sholkovitz E R, Boyle E A & Price N B, *Earth Planet Sci Letts*, 40 (1978) 130.