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ACKNOWLEDGEMENTS. We thank the anonymous reviewers for constructive comments and Francis McCubbin of University of New Mexico for providing the Durango apatite standard. We acknowledge support provided by Dipak Panda and Lalit Shukla during EPMA and NanoSIMS analysis respectively.

Received 6 January 2015; revised accepted 17 December 2015

doi: 10.18520/cs/v110/i8/1536-1539

Carbon isotopic composition of suspended particulate matter and dissolved inorganic carbon in the Cochin estuary during post-monsoon

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Detailed measurements of carbon (C) isotopic composition in dissolved inorganic ($\delta^{13}C_{DIC}$) and particulate organic ($\delta^{13}C_{POC}$) fractions were conducted at 18 stations in the Cochin estuary during the post-monsoon season. In general, C biogeochemistry of different regions of the Cochin estuary appears to be regulated by different sources and processes. The northern zone of the estuary appears to be influenced primarily by mixing of sea water enriched in $^{13}C_{POC}$ and $^{13}C_{DIC}$, and river run-off depleted in the same. In contrast, the southern zone of the estuary was found to be greatly influenced by local terrestrial sources. Relatively depleted $^{13}C_{POC}$ in the freshwater Vembanad lake compared to the main estuary suggests inputs from terrestrial sources along with *in situ* productivity.

Keywords: Carbon isotopic composition, estuary, particulate organic matter, terrestrial sources.

ESTUARIES and lakes are emerging as prominent sources of CO_2 (refs 1–7), globally as they are estimated to emit 0.43 Pg C y^{-1} and 0.14 Pg C y^{-1} respectively[8,9]. An updated estimate shows that inner estuaries, salt marshes and mangroves around the world[10] emit ~0.50 Pg C y^{-1}, while Indian estuaries[11] emit 1.92 Tg C y^{-1}. Estuaries which are in contact with large human settlements sustain high rates of CO_2 emission[6,12–15] due to enhanced mineralization of river-borne particulate organic matter (POM) and heterotrophy[1,3]. The sources of POM in the estuaries are both allochthonous and autochthonous. Allochthonous sources include terrestrial organic matter (TOM), domestic and industrial run-off, and marine inputs, whereas autochthonous sources comprise materials from estuarine sources. Consequently, the dissolved inorganic carbon (DIC) pool in estuaries also gets amended by both these influences. It is thus important to understand the sources and pathways of POM to decipher its role in carbon (C), nitrogen (N) and oxygen (O) cycles within estuaries and coastal areas, and its overall importance in the global C cycle[16].

Although several studies have been conducted on plankton dynamics and POM in estuaries around the world[17–20], a full understanding of the sources, fate and transformations of POM in tropical estuarine systems is lacking. Previous studies in Indian estuaries have mainly focused on nutrients biogeochemistry, plankton dynamics, trophic status, CO_2 flux, etc. with the exception of some studies related to C isotopic composition of DIC and POM[4,21,22]. Since isotopic fractionation occurring during each step of C cycling leaves the substrate and product pools with distinguishable isotopic ratio, the stable C isotopic compositions of POM ($\delta^{13}C_{POC}$) and DIC ($\delta^{13}C_{DIC}$) can be used as proxy to understand various sources and related biogeochemical processes in the C cycle.

The present study provides detailed measurements of $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ in the Cochin estuary, one of the important estuaries in India, situated at the interface of the southeastern Arabian Sea and major river systems. The total annual freshwater input to this estuary is about 20,000 Mm^3, making it the largest wetland along the west coast of India[23]. The seasonal variability and tidal fluctuations in the estuarine salinity play a significant role in the biogeochemistry of this backwater ecosystem[24]. The Cochin estuary is a pivot for plethora of TOM and conse-

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quently a source of CO_2 (refs 7, 25, 26). The reported CO_2 flux from the Cochin estuary (0.16 Tg C y^{-1}) corresponds to ~8% of total CO_2 emission from Indian estuaries[11]. Therefore, an investigation on C sources, sinks and transformations from such estuarine systems is highly desirable.

Samples were collected during the post-monsoon (December 2012) for $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ at 15 stations across the salinity gradient within the estuary and three stations in the freshwater Vembanad Lake, located upstream of the estuary and separated by a dam (Figure 1). Samples for $\delta^{13}C_{DIC}$ and pH were collected in 125 ml glass bottles and poisoned immediately with saturated $HgCl_2$ (0.6% v/v) to stop microbial activity. Gas-tight caps were placed on the bottles which were covered with Parafilm. The samples were stored in the dark until further analysis pH and total alkalinity (TAlk)[27] were measured in the laboratory using a potentiometric titrator (907 Titrando, Metrohm, Switzerland) calibrated on the NBS scale[28]. These laboratory pH values on NBS scale were first converted to pH *in situ* and then to total scale. Analytical precision of pH for the freshwater samples was ±0.008, and for the rest it was ± 0.005. DIC and pCO_2 were computed using measured temperature, salinity, TAlk and *in situ* pH (total scale). The precision for pCO_2 was 9–13 μatm.

Samples for $\delta^{13}C_{POC}$ and POC were filtered through pre-combusted 47 mm GF/F filters (400°C for 4 h) and dried overnight at 50°C. Prior to the analysis, samples were fumigated overnight with concentrated HCl in a desiccator to remove the inorganic C followed by oven-drying at 50°C. Measurements of $\delta^{13}C_{POC}$ and POC were carried out using a continuous flow isotopic ratio mass spectrometer (Thermo Delta V plus) attached to a Flash 2000 elemental analyzer. IAEA CH-3 cellulose ($\delta^{13}C_{V\text{-}PDB}$ = –24.724‰ and C content = 44.4%) was used as the isotopic as well as POC concentration standard with isotopic reproducibility better than 0.06‰.

The measurements for $\delta^{13}C_{DIC}$ were performed using continuous-flow isotopic ratio mass spectrometer (Thermo Delta V plus) attached to a Gas Bench system. For the measurements of $\delta^{13}C_{DIC}$, samples were treated with 100% orthophosphoric acid and kept in the temperature bath (28°C) for 18 h. $\delta^{13}C$ was calculated based on the standard equation

$$\delta^{13}\mathrm{C}(‰) = \left(\frac{R_{\mathrm{Sample}} - R_{\mathrm{V\text{-}PDB}}}{R_{\mathrm{V\text{-}PDB}}} \right) \times 10^3.$$

The laboratory standard used for $\delta^{13}C_{DIC}$ was $NaHCO_3$ ($\delta^{13}C_{V\text{-}PDB}$ = –11.4‰). The analytical reproducibility for replicate standards was better than 0.1‰.

Table 1 shows the environmental parameters along with DIC, pCO_2, POC, $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ in the Cochin estuary during the study period. Salinity and pH in the estuary ranged from 3.39 to 32.31 and 7.050 to 8.058 respectively. The absence of rainfall and high-tide phase during sampling resulted in relatively higher salinity and pH than those of pre-monsoon[29]. Supersaturated CO_2 conditions prevailed in most of the stations, with the highest pCO_2 of 7229 μatm recorded in Vembanad Lake (station 17, Table 1), probably due to supply of allochthonous organic matter and its degradation[25,26]. The sources of allochthonous matter include both terrestrial and marine inputs, which consists of pelagic, benthic and chemoautotrophic primary producers[22]. The pCO_2 values observed in this estuary during the present study, a relatively dry period, are much lower than high-flow periods as many Indian estuaries during the latter period exhibit up to 90% mineralization of TOM loads[7,30,31].

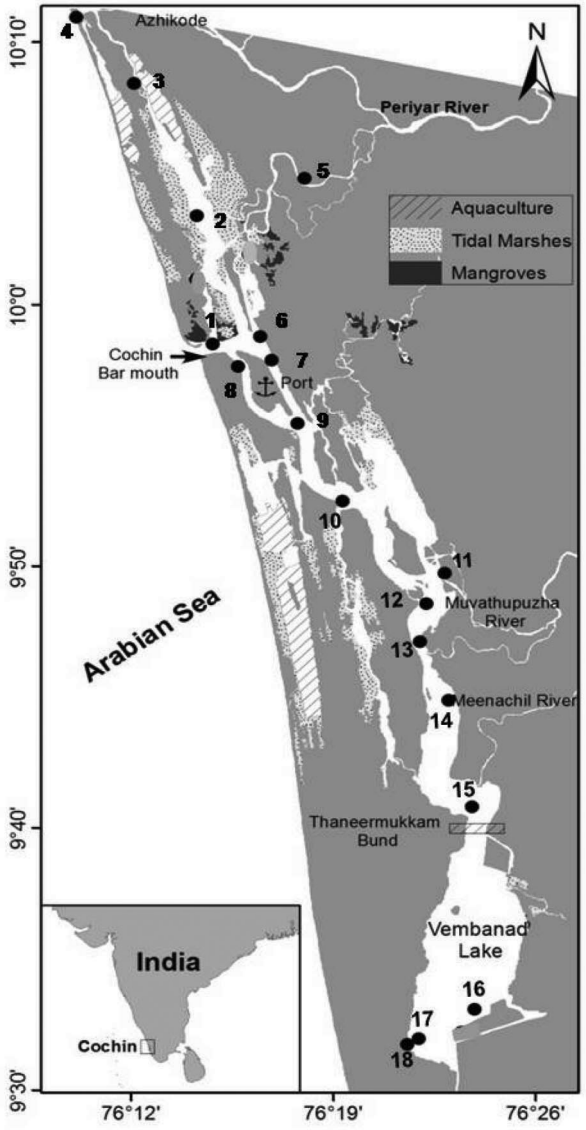

Figure 1. Sampling locations in the Cochin estuary.

Table 1. The environmental parameters along with POC, $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ at different stations during the study period

Station no.	Salinity	pH	DIC (μmol/kg)	pCO_2 (μatm)	POC (μm)	$\delta^{13}C_{POC}$ (‰)	$\delta^{13}C_{DIC}$ (‰)
1	32.31	8.058	1539	439	20.15	–22.49	0.79
2	22.99	7.570	1233	1946	49.37	–24.11	–3.12
3.	24.47	7.619	1355	1170	28.45	–25.11	–2.17
4	29.84	7.964	1461	536	24.65	–23.31	0.22
5	3.39	7.050	697	1145	53.37	–28.66	–6.34
6	9.37	7.547	1297	570	75.63	–25.69	–3.69
7	24.23	8.017	1243	545	74.23	–21.69	–0.23
8	25.41	7.914	1584	602	66.94	–23.04	–0.38
9	32.12	7.968	1275	629	56.24	–21.59	0.48
10	25.46	7.833	1029	1094	35.45	–23.16	–1.12
11	20.17	7.527	522	1198	40.55	–24.30	–1.92
12	10.46	7.202	546	1704	24.18	–28.73	–5.35
13	11.12	7.130	439	242	44.37	–28.12	–4.13
14	9.21	7.896	405	786	19.05	–28.31	–2.60
15	9.77	7.364	422	1767	24.56	–29.48	–2.73
16	1.92	6.994	403	5552	36.56	–31.45	–3.06
17	1.95	6.414	343	7229	19.37	–33.73	–4.93
18	1.89	6.413	473	6966	35.98	–33.40	–3.81

The high POC content in the Cochin estuary is an indicator of both TOM loading and enhanced primary productivity (Table 1). The observed POC concentrations in the Cochin estuary (19.05–75.63 μM) are comparable to those observed in the Zuari estuary (40–130 μM)[22] and are relatively lower than those of the Thames estuary (40.1–1015 μM)[16]. During the present study, $\delta^{13}C_{POC}$ in the Cochin estuary ranged between –33.73% and –21.59‰ (Table 1). Typically, $\delta^{13}C_{POC}$ values from –34% to –26‰ are indicative of riverine origin[32–34], whereas $\delta^{13}C_{POC}$ for marine phytoplankton and sewage ranges from –23% to –17‰ (refs 18, 33, 35, 36), and –29% to –23‰ (ref. 18) respectively. Some studies have reported $\delta^{13}C$ values of riparian C3 plants ranging between –26% to −28‰ (refs 37, 38). Similarly, the sources of DIC can also be identified using $\delta^{13}C_{DIC}$ as proxy. The $\delta^{13}C_{DIC}$ observed during the present study (–6.34% to +0.78‰) is comparable with the Godavari River delta during pre-monsoon period[4], and is relatively enriched compared to that of the Hooghly estuary during post-monsoon[31,36].

The downstream of the estuary is in continuous contact with the coastal Arabian Sea and interchanges their physio-chemical properties at the meeting interface. The surface average values of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ of the coastal Arabian Sea during post-monsoon are +0.81‰ and –21.65‰ respectively[29]. Hence, relatively higher values of $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ in the stations with low pCO_2 and high salinity possibly indicate dominant contributions from coastal waters. $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ at these stations are closer to isotopic composition of marine DIC and phytoplankton. Similar patterns of POC and DIC, as observed in this estuarine system, have also been observed in other estuaries around the world[18,33,35–38]. This kind of isotopic enrichment of $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ in the estuarine systems during the dry season occurs due to upstream transport of marine POC and DIC during high tides which dominate the estuarine circulation[22]. It is noteworthy that sampling for the present study was performed during high-tide phase.

However, source identification of DIC and POM may be difficult at locations or regions where multiple sources with overlapping isotopic signatures contribute in different proportions. In such cases, construction of a conservative mixing curve and deviations of actual values from the mixing line may be helpful. The present study followed two different mixing curve approximations for DIC[39] and POM[40,41]. For these models, Periyar river inlet point (major river draining into the estuary – station 5) and Barmouth (station 1) were considered as end-members of freshwater and sea water respectively. Since various parts of the estuary, particularly the southern part, receive freshwater inputs from many small rivers and tributaries, consideration of Periyar inlet as the only freshwater end-member may be an approximation. For a better understanding of the processes in this estuary, stations were classified into three major zones: stations 1–9 (northern zone; Periyar river is the major freshwater source), 10–15 (southern zone; freshwater inputs from various sources), and 16–18 (Vembanad lake, a freshwater lake).

Figure 2 *a* and *b* shows the conservative mixing curve of DIC and $\delta^{13}C_{DIC}$ respectively, along with their respective actual values and salinity in three different zones of the Cochin estuary. The stations in the northern zone are, in general, close to the conservative mixing line,

except at two stations. The stations in southern zone are characterized by lower $\delta^{13}C_{DIC}$ and DIC relative to the respective conservative mixing values with exception of two stations in the low saline region. The possible reason for low $\delta^{13}C_{DIC}$ and DIC in these stations might be the dominant contribution from terrestrial sources. Similarly, the conservative mixing approximation for $\delta^{13}C_{POC}$ is also in agreement with the high TOM loading in the southern zone of the Cochin estuary (Figure 3). At mesohaline regions in the southern zone, mixing of both TOM and marine phytoplankton would have resulted in $\delta^{13}C_{POC}$ ranging from –24.30% to –23.16‰. Similarly, the observed $\delta^{13}C_{POC}$ (−29.48% to –28.12‰) in the low saline regions of the southern zone are likely a combined isotopic signature of freshwater phytoplankton ($\delta^{13}C \sim$ –30‰) and humic-rich sediment ($\delta^{13}C \sim$ –26‰)[41]. Both DIC and POC mixing models indicate that the Vembanad Lake carries signatures of freshwater phytoplankton and *in situ* primary production.

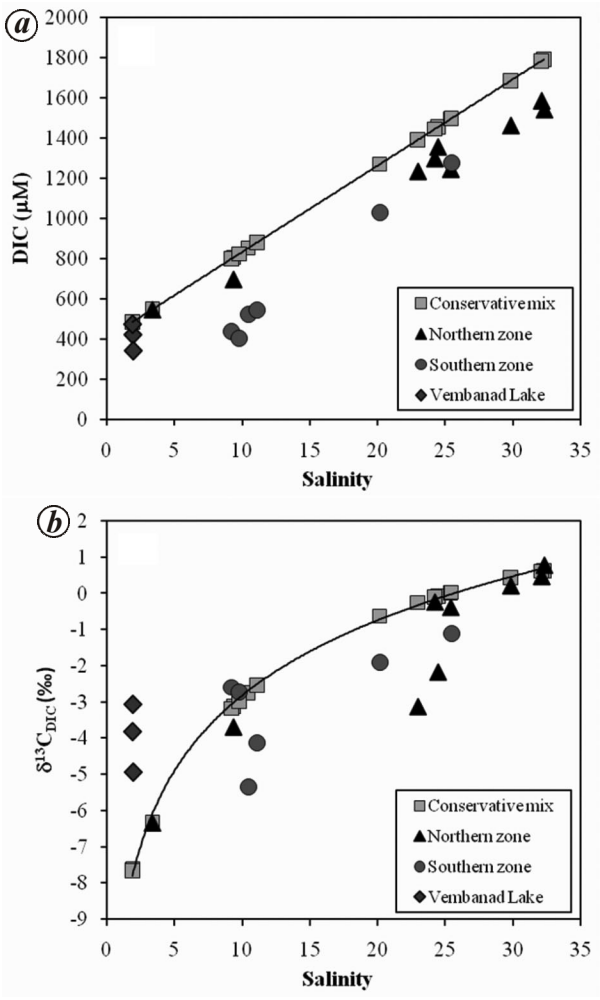

Figure 2. Conservative mixing curves of (***a***) dissolved inorganic carbon concentration; (***b***) $\delta^{13}C_{DIC}$ for the Cochin estuary.

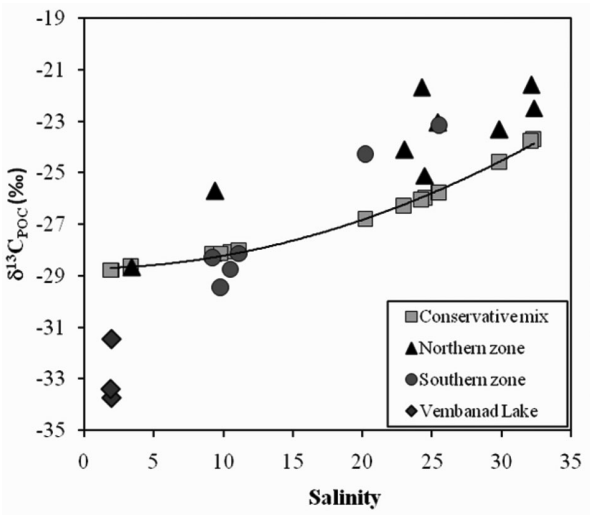

Figure 3. Conservative mixing curve of $\delta^{13}C_{POC}$ for the Cochin estuary.

To summarize, C biogeochemistry of different parts of the Cochin estuary appeared to be influenced by different sources and processes. The northern zone is influenced by mixing of sea water enriched in $^{13}C_{POC}$ and $^{13}C_{DIC}$ and river run-off depleted in the same. C dynamics in the southern zone of the estuary, however, is found to be greatly affected by local river run-off. The results also point towards the overlapping and mixed signatures of different processes in the southern zone. Additionally, the influence of tidal-driven invasion of the coastal waters is substantial in determining $\delta^{13}{}_{POC}$ as well as $\delta^{13}{}_{DIC}$ of the estuarine C pool. To understand the cycling and transformations of C in this complex estuary, a well-structured and long-term isotopic measurement of POC, DIC and DOC is recommended.

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ACKNOWLEDGEMENTS. We thank the Secretary, Ministry of Earth Science (MoES); Director, Centre for Marine Living Resources and Ecology and R. Ramesh, Physical Research Laboratory for support. We also thank Dr K. K. Balachandran (NIO, Cochin, Kerala) for technical discussions and field support. This study was funded by MoES and ISRO-GBP, Department of Space, Government of India.

Received 11 May 2015; revised accepted 4 January 2016

doi: 10.18520/cs/v110/i8/1539-1543