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Appraisal of nutrient distribution in the surface water and bed sediments of a small mountainous river

Prince George · Sabu Joseph

Abstract A total of 42 (21 surface water and 21 bed sediments) samples were collected from upstream to downstream stretches of Meenachil river during pre-monsoon (PRM), monsoon (MON) and post monsoon (POM) seasons. DOC in water showed increasing trend spatially while temporal study illustrates high mean value during PRM (1.58 ppm) followed by POM (0.97) and MON (0.36). Spatial assessment of elements such as Ca, Mg, K and Na in sediments reveals erratic trend during different seasons, while total phosphorous showed escalating trend signifying abrupt addition from anthropogenic sources. Based on characteristic carbon to nitrogen ratio, the study demonstrates significant control of macrophyte in terrestrial organic matter accumulation along downstream stations.

Keywords Small mountainous river · Water-sediment · DOC · Meenachil river

Introduction

Materials transported by rivers are key components of the hydrological balance, the sediment balance, the nutrient balance and the biodiversity of aquatic system (Meybeck 2003). Intensification of agricultural system in developing countries with high population growth rate (Matthews 1994) is necessary to support humanity while population rise is likely to double by the end of the next century (Vitousek et al. 1997). In addition to fertiliser loss from agricultural lands, sewage, combustion products from fossil fuel burning and extensive oxidation of natural organic matter from forest clearing will generate additional flows of nutrients in waters draining the continents (Peterson and Melillo 1985). All abrupt changes happening due to urbanisation related activities could be traced by systematic evaluating the water and sediment quality characters in the aquatic system. Extensive study of hydrological process in mountain catchments (Gallart et al. 2002) illustrates that sediment transport is a complex phenomenon resulting from both geomorphic processes such as physical weathering, runoff generation at the catchment scale, rainfall inputs and the antecedent conditions while others (Regüés et al. 1995) point out the control of seasonal processes in modifying the characteristics of the surface regolith and physical weathering processes with changing seasons. Studies also suggest that river bed sediments provide a key 'missing link' between sediment- associated diffuse sources delivered to the stream channel during rainfall events and the subsequent impacts at times of ecological sensitivity (Jarvie et al. 2005).

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Study area

The Meenachil river basin (MRB) (n = 7th, L = 78 km, A = 1272 km^2), located in central Kerala, lies between 9° 25′ to 9° 55′ N latitudes and 76° 30′to 77° 00′ E longitudes. This tropical mountainous river (Padmalal et al. 2008) originates from the Western Ghats, flows in the E-W direction (Fig. 1), exhibits a dendritic drainage pattern and splits into a number of distributaries in the lowlands and finally debouch into the Vembanad lake. Precambrian metamorphic rocks such as quartzite, charnockite, garnet-iferous biotite gneiss and pink/grey granite are seen in MRB catchment. The major soil type is well drained lateritic soils, while Quaternary formations and recent sediments of coastal sands along with alluvium were seen in lower reaches of river catchment (GSI 2002).

The basin fall under tropical humid climate with an average annual rainfall around 3000 mm and annual temperature fluctuates between 24 and 32 °C. The river basin experience southwest (SW) monsoon starting from June and lasts till August and the northeast (NE) monsoon from October to the end of November, having an average rainfall recharge of 4.5%, while sediment load composes

of about 0.02×10^6 t (Chandramohan and Balchand 2010). The upland catchment consists predominantly of rubber plantation (*Hevea brasiliensis*), mixed vegetation of plantain (*Musa sapientum*), coconut (*Cocos nucifera*) and tapioca (*Manihot esculenta*) while catchments in lower reaches of river system mainly compose of paddy (*Oryza sativa*) cultivation along north Kuttanad area (Fig. 2).

Materials and methods

A total of 42 samples (21 water samples and 21 bed sediment samples) were collected from Meenachil river upstream to downstream during August 2013 to April 2014 covering three seasons (pre-monsoon (PRM), monsoon (MON) and post monsoon (POM)). Non-purgable organic carbon (NPOC) of water samples, in present work treated as dissolved organic carbon (DOC), was estimated using TOC-analyser (TOC-V$_{CSH}$, Shimadzu). Determination of calcium (Ca), magnesium (Mg), potassium (K), sodium (Na) and total phosphorus (TP) were done using ICP-AES (Thermo Electron Iris Intrepid II
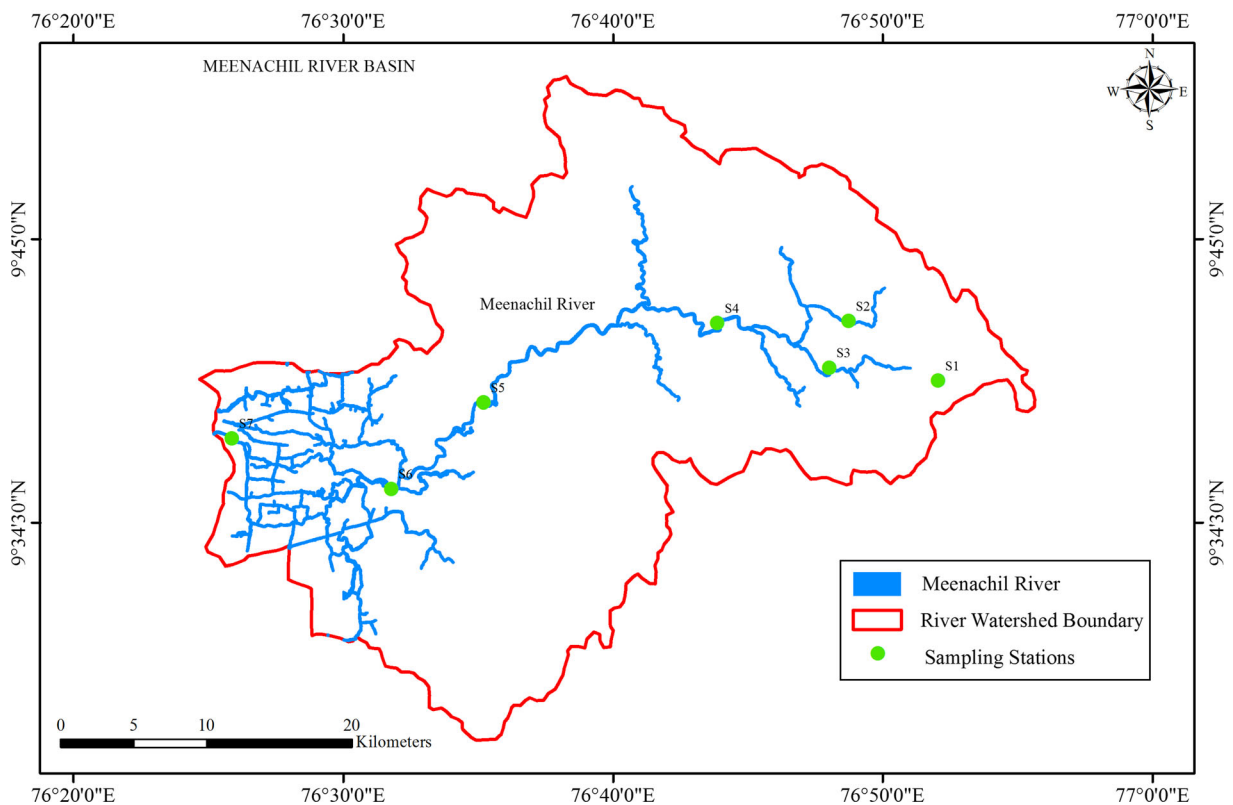
Fig. 1 Portrait of sampling locations
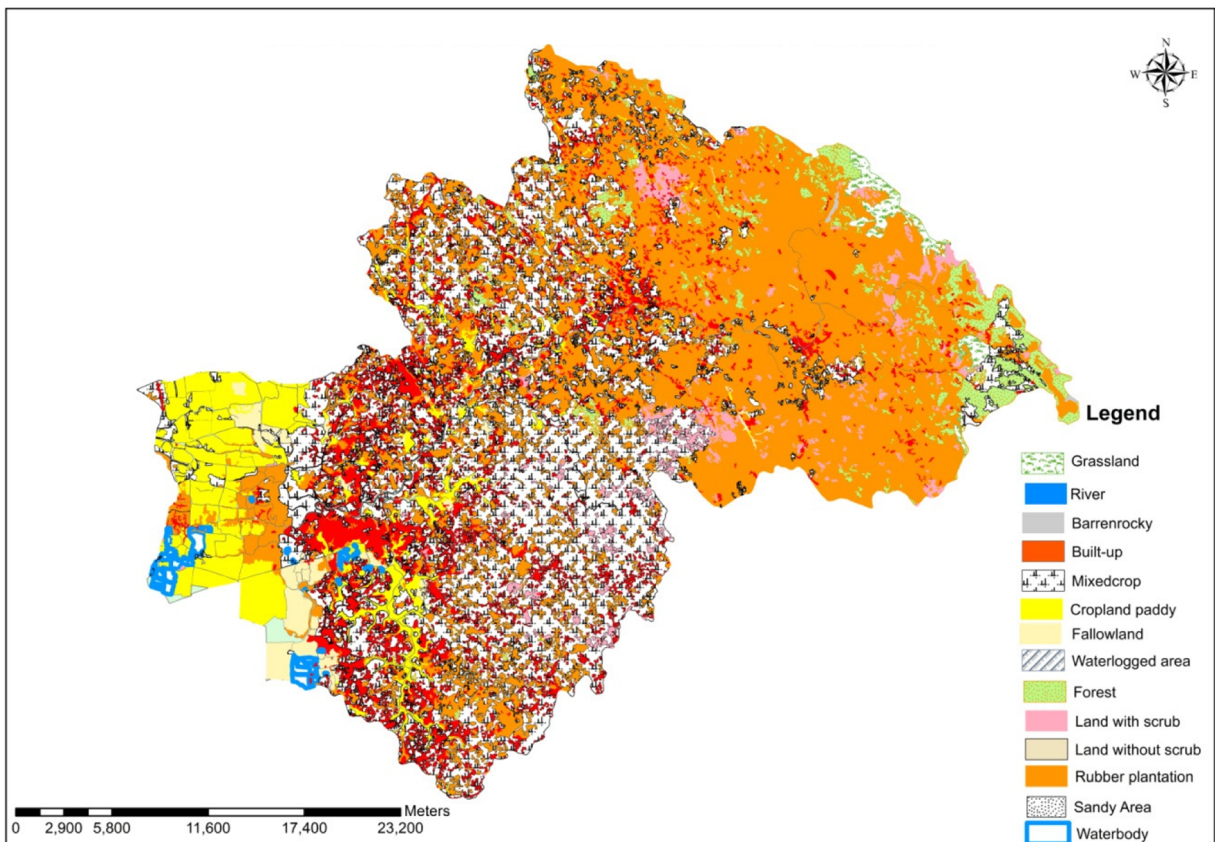
Fig. 2 Land use map of Meenachil river basin during 2007

XSP DUO) for both water and sediment samples. However, for sediment analysis, wet sediments were homogenised and air-dried. Dried sediments were fine powdered using ball micromill (Fritsch, Pulverisette 7) and digested. Liquid from the digested solid samples was then used for further analysis. Total carbon (TC) and total nitrogen (TN) concentrations in dried sediment were determined using CHNS analyser (Elementar Vario EL III). Hereafter, the concentrations of element (X) in water and sediment samples correspond to X_{wat} and X_{sed} respectively.

Results and discussion

Results

Water chemistry

Spatial evaluation reveals that most of the water quality parameters show intensification toward downstream stations, while temporal study illustrates that amplification in concentrations occurs mainly during PRM. Mean PRM concentrations of Ca_{wat} varied between 8.02 (PRM) and 6.02 ppm (MON), while Mg_{wat} (2.48), Na_{wat} (13.98) and K_{wat} (3.78) show maximum value of during PRM (Table 1). From the water quality results, it is clear that monsoon rainfall strictly control the hydrochemistry of this small mountainous river system. The mean DOC_{wat} shows highest value during PRM (1.58 ppm) followed by POM (0.97) and MON (0.36). The absence of significant correlations for DOC_{wat} during MON points toward the strong control of rainfall either by dilution or flushing the organic carbon in river.

Sediment chemistry

Ca_{sed} concentrations ranged from 1.18 to 2.08, 1.03 to 2.43 and 1.41 to 2.68 ppm during PRM, MON and POM, respectively, typifying no pronounced variation both spatially and temporally. Mg_{sed} concentrations ranged 1.25 to 2.76, 1.7 to 2.67 and 0.76 to 1.84 ppm

Table 1 Water quality variations during different seasons

|	PRM			MON			POM		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Ca_{wat}	3.17	17.67	8.02	4.64	7.35	6.02	6.47	8.36	7.40
Mg_{wat}	0.44	6.93	2.48	0.77	1.32	1.01	0.82	4.64	1.79
Na_{wat}	3.98	48.92	13.98	2.29	6.25	4.01	3.40	12.10	6.51
K_{wat}	1.40	8.73	3.78	0.51	1.31	0.93	0.90	2.04	1.45
TP_{wat}	0.01	0.07	0.04	0.01	0.10	0.05	0.01	0.12	0.05
DOC_{wat}	0.80	3.38	1.58	0.13	0.81	0.36	0.36	4.19	0.97

All values are in ppm

during PRM, MON and POM, respectively. Spatial evaluation showed depleting trend in K_{sed} concentrations while Na_{sed} concentrations reveal erratic trend temporally. TP_{sed} ranged from 0.02 to 0.14, 0.02 to 0.12 and 0.02 to 0.11 ppm during PRM, MON and POM, respectively, indicating increasing concentrations spatially. Representations of these variations are given in Fig. 3. This variability could arise due to that various factors like erosional and depositional processes operating within river channels have the potential to create bed sediments that display a high degree of spatial heterogeneity with fine particles accumulating in areas of reduced flow velocity such as backwaters and macrophyte spread area (Clarke and Wharton 2001). Moreover, various studies (John et al. 2009) demonstrated extensive and impenetrable dense mono-specific stands of *Ischaemum travancorense*, *Hymenachne acutigluma*, *Phragmites karka*, *Typha angustata* and *Eichhornia crassipes* pausing considerable threat to aquatic ecosystem in the Kuttanad area (lower catchment areas of MRB).

Discussion

Results suggest that concentrations of Ca, Mg, Na and K exhibit no significant correlation with surface water and bed sediment (Table 2). However, TP_{sed} and TP_{wat} show significant correlation during PRM ($r = 0.78$, $P < 0.05$), MON ($r = 0.85$, $P < 0.05$) and POM ($r = 0.93$, $P < 0.01$). The bed sediment surveys (Jarvie et al. 2005) have shown that equilibrium phosphorus concentration (EPC_0) values are correlated with soluble reactive phosphorus (SRP) concentrations analysed for the overlying water at the time of bed-sediment sampling. Spatial evaluation demonstrates amplification of TP_{wat}

concentration toward the downstream stretches of river system. In general, geologic or natural availability of phosphorus (a part of the grand geotectonic denudation-uplift cycle) is slow, and low solubility of phosphates and their rapid transformation to insoluble forms make the element commonly the growth-limiting nutrient, especially in aquatic ecosystems (Smil 2000). It is evident that in rampant agricultural activities prevailing along the downstream catchments especially in Kuttanad, the rice bowl of Kerala is famous for 'low land agriculture'. Leaching of excess fertilisers from these agricultural fields has got vital role in controlling phosphate dynamics in downstream stations. However, significant rise of TP_{wat} in highlands (S4 station) in PRM and TP_{sed} during MON (S4 station) suggests the contribution of leachate from widespread rubber plantations (Kumar 2005) in the upland catchment area (Fig. 4). Amplification of TP_{wat} in runoff has got wide repercussion such as increased rate of fertiliser usage (Römkens and Nelson 1974; Sims et al. 1998), watershed soil characters (Vaithiyanathan and Correll 1992; Sharpley et al. 1996) and dominance of plantation (Chen and Lin 2016). Apart from above-mentioned, characteristics within the watershed boundary (of MRB) and several other issues addressed with respect to microbial contamination (Vincy et al. 2015) also have vital consequences in defining the water quality in downstream stretches of the riverine system.

It is noted that Ca_{wat} shows significant correlation with Mg_{wat} throughout the study period irrespective of season that indicates role of weathering process in controlling the water chemistry. Evaluation of DOC_{wat} reveals that during PRM, significant correlation with Ca_{wat} ($r = 0.8$, $P < 0.05$, $n = 42$), Mg_{wat} ($r = 0.85$, $P < 0.05$), Na_{wat} ($r = 0.9$, $P < 0.01$), K_{wat} ($r = 0.9$, $P < 0.01$) and TP_{sed}
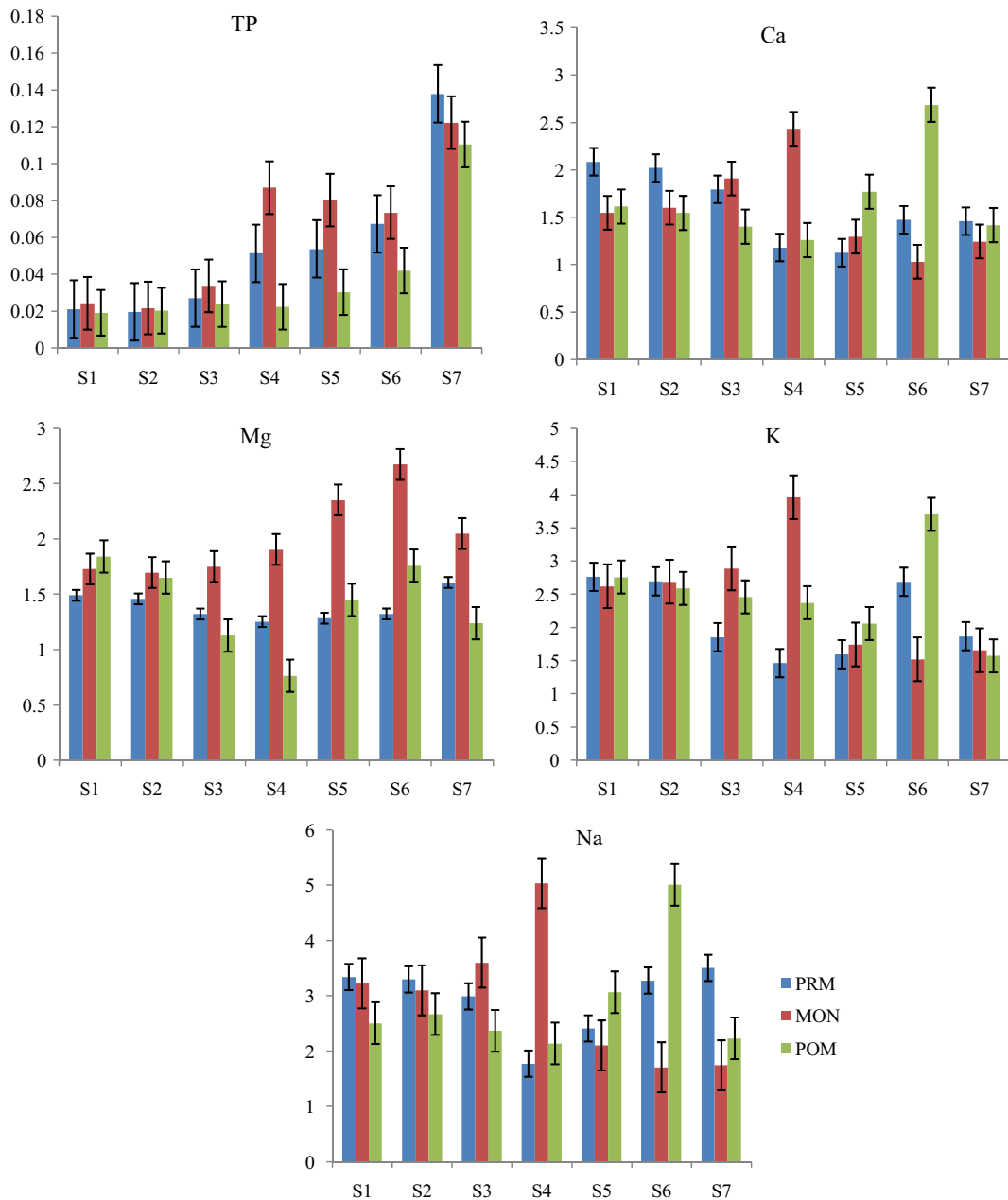
Fig. 3 Spatial and temporal variations of different sediment parameters (in mmol)

($r = 0.89$, $P < 0.01$) was noted, while POM result shows significant correlation with Mg_{wat}($r = 0.9$, $P < 0.01$), Na_{wat} ($r = 0.81$, $P < 0.05$), TP_{wat}($r = 0.82$, $P < 0.05$) and TP_{sed} ($r = 0.93$, $P < 0.01$).

Our DOC_{wat} results convey the role played by increased temperature (Freeman et al. 2001; Worrall and Burt 2004) in tropical regions especially during PRM.

Relationship of K_{sed} reveal that contribution of potassium along upstream stations is a possible outcome related to weathering of geological features (such as K-feldspar and biotite) existing in the basin (Fig. 5). This weathering can be considered as a dominant lithological factor controlling the availability of potassium in river sediments. Similarly, studies have suggested central role

Table 2 Correlation matrix for water and sediment samples during PRM (a), MON (b) and POM (c)

	Ca_{wat}	Mg_{wat}	Na_{wat}	K_{wat}	TP_{wat}	DOC_{wat}	Ca_{sed}	Mg_{sed}	K_{sed}	Na_{sed}	TP_{sed}
(a)											
Ca_{wat}	1										
Mg_{wat}	*0.996**	1									
Na_{wat}	*0.944**	*0.965**	1								
K_{wat}	*0.976**	*0.990**	*0.962**	1							
TP_{wat}	*0.765**	*0.766**	*0.704*	*0.757**	1						
DOC_{wat}	*0.805**	*0.849**	*0.903**	*0.901**	0.625	1					
Ca_{sed}	−0.540	−0.517	−0.306	−0.526	−0.566	−0.272	1				
Mg_{sed}	0.318	0.371	0.590	0.378	0.008	0.564	0.501	1			
K_{sed}	−0.226	−0.253	−0.141	−0.339	−0.496	−0.345	*0.761**	0.398	1		
Na_{sed}	0.202	0.216	0.384	0.197	−0.165	0.337	0.671	*0.771**	0.727	1	
TP_{sed}	*0.970**	*0.987**	*0.975**	*0.991**	*0.768**	*0.893**	−0.504	0.431	−0.325	0.182	1
(b)											
Ca_{wat}	1										
Mg_{wat}	*0.868**	1									
Na_{wat}	−0.389	−0.109	1								
K_{wat}	−0.258	−0.133	*0.897**	1							
TP_{wat}	−0.560	−0.428	*0.922**	*0.918**	1						
DOC_{wat}	−0.392	−0.322	0.476	0.434	0.494	1					
Ca_{sed}	0.740	*0.885**	−0.336	−0.328	−0.608	−0.575	1				
Mg_{sed}	−0.298	−0.435	0.638	*0.845**	*0.845**	0.359	−0.621	1			
K_{sed}	0.681	*0.782**	−0.469	−0.431	−0.691	−0.655	*0.978**	−0.667	1		
Na_{sed}	0.732	*0.812**	−0.464	−0.405	−0.685	−0.640	*0.980**	−0.632	*0.996**	1	
TP_{sed}	−0.334	0.005	*0.976**	*0.877**	*0.849**	0.469	−0.181	0.528	−0.315	−0.313	1
(c)											
Ca_{wat}	1										
Mg_{wat}	*0.755**	1									
Na_{wat}	*0.875**	*0.967**	1								
K_{wat}	*0.952**	*0.841**	*0.935**	1							
TP_{wat}	0.675	*0.956**	*0.924**	*0.835**	1						
DOC_{wat}	0.564	*0.909**	*0.811**	0.642	*0.822**	1					
Ca_{sed}	0.111	0.154	0.208	0.194	0.291	−0.225	1				
Mg_{sed}	−0.492	−0.098	−0.195	−0.420	−0.048	−0.200	0.623	1			
K_{sed}	−0.286	−0.348	−0.328	−0.280	−0.214	−0.611	*0.770**	0.517	1		
Na_{sed}	0.132	0.125	0.200	0.214	0.274	−0.267	*0.992**	0.550	*0.782**	1	
TP_{sed}	0.652	*0.976**	*0.907**	0.754	*0.925**	*0.973**	−0.015	−0.127	−0.486	−0.052	1

*Correlation is significant at the 0.05 level (two-tailed); **correlation is significant at the 0.01 level (two-tailed)

The values italicized demonstrate level of significance/strong correlation between the corresponding variables

played by catchment geological formation (Mesozoic marls, draining badlands) of being the important sediment source (Francke et al. 2008). Meanwhile, increasing trend of K_{wat} toward downstream stations during all seasons is due to contamination from anthropogenic sources such as contribution of potassium from fertiliser's, leachate from plantations and cultivable lands.
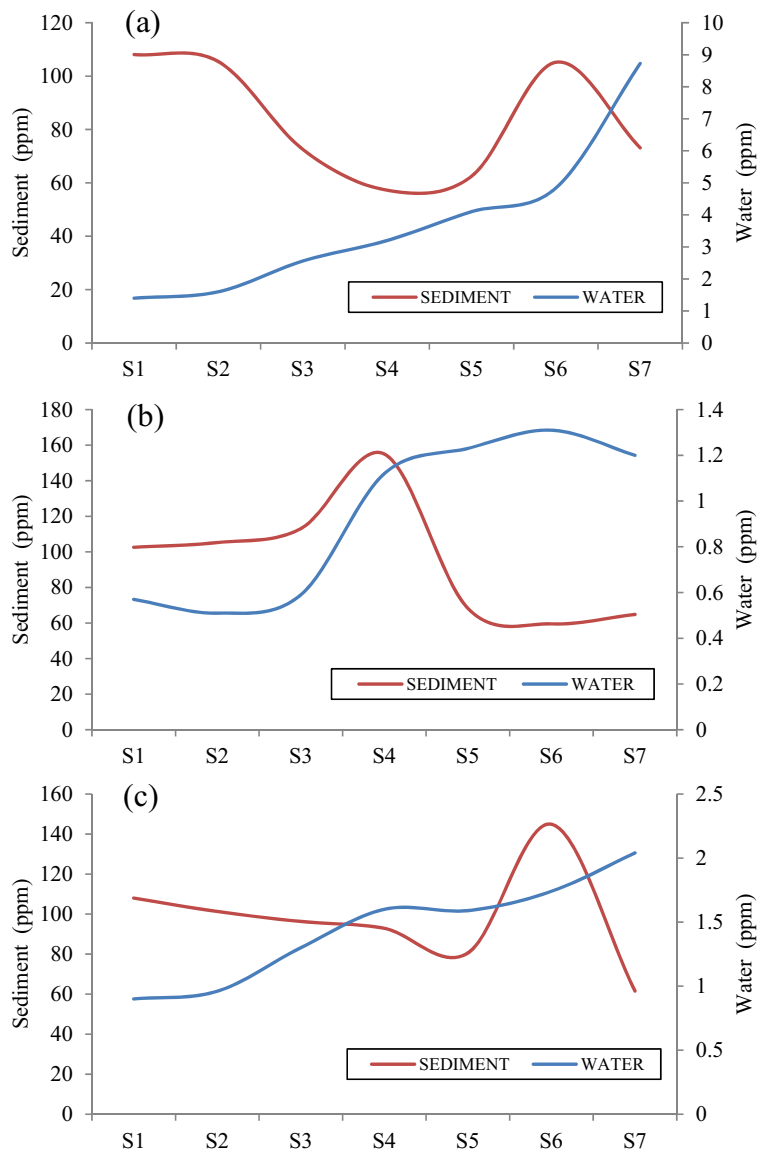
Fig. 4 Total phosphorus concentration in sediment and water during PRM (**a**), MON (**b**) and POM (**c**)
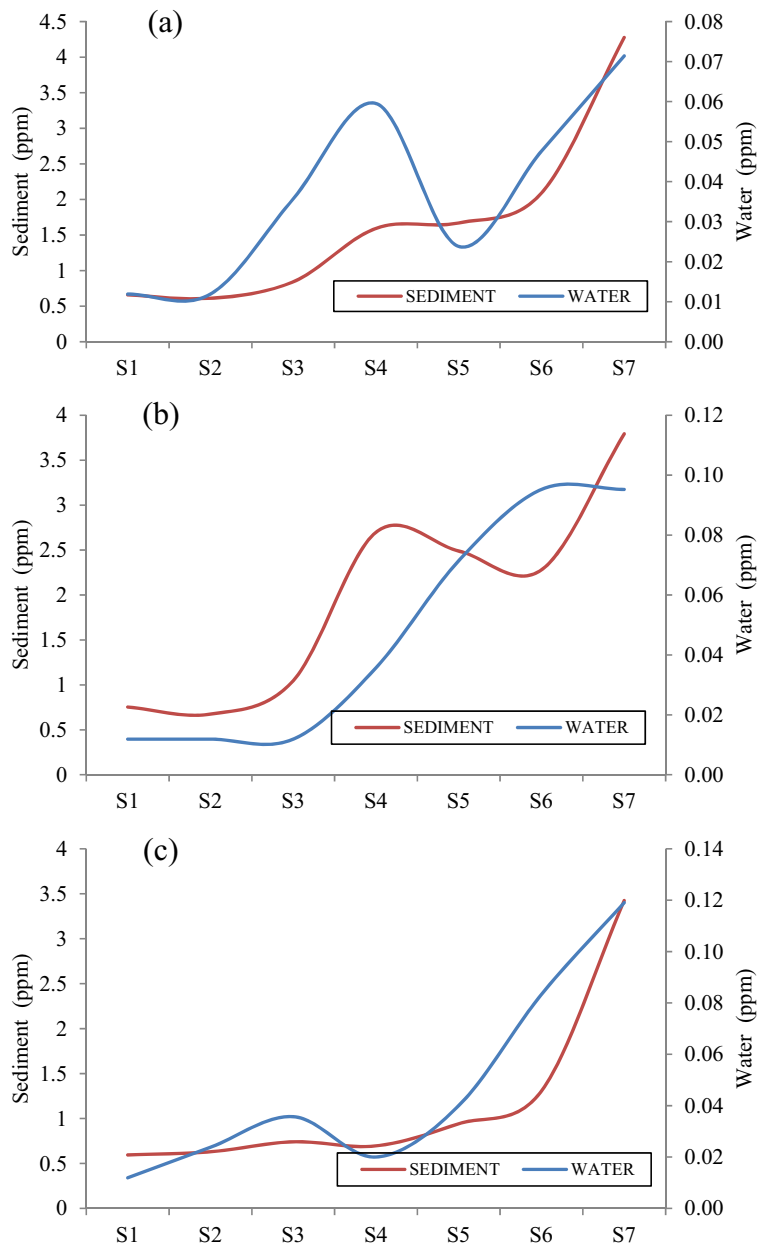
Mean values (wt%) of Ca_{sed} (PRM 0.06, MON 0.06 and POM 0.07), Mg_{sed} (PRM 0.03, MON 0.05 and POM 0.03), K_{sed} (PRM 0.08, MON 0.1 and POM 0.1) and Na_{sed} (PRM 0.07, MON 0.07 and POM 0.07) indicate an overall depletion of these elements relative to those in Upper Continental Crust (Taylor and McLennan 1985), while mean molar ratios of $(K/Na)_{sed}$ during PRM (0.73), MON (0.85) and POM (0.9) suggest multiple source for K in river sediments apart from weathering.

$(C/N)_{sed}$ values varied widely both spatially and temporally. $(C/N)_{sed}$ ratio ranged between 6.12–14.85, 8.92–19.83 and 7.98–14.776 during PRM, MON and POM, respectively (Table 3). High $(C/N)_{sed}$ values noted in downstream stations are due to the various factors such as lithology and agricultural activities prevalent in those stretches. Highest $(C/N)_{sed}$ value (S6, Railway station area) observed during MON season is due to abrupt rise in carbon concentrations. This massive rise in carbon values was mainly due to bed rock lithology

Fig. 5 Potassium concentrations in sediment and water during PRM (**a**), MON (**b**) and POM (**c**)

comprising of recent marine deposits during Holocene period and fluvial deposits (GSI 2002; Ajaykumar et al. 2010). Various studies suggest that C/N value higher than 15 indicates significant role of terrestrial organic matter in controlling the aquatic system (Meyers 1994). The above statement is in agreement with our results, exposing the terrestrial influence in (S6 and S7) during MON season, which has C/N value above 15. Macrophyte bloom evident in S6 characterises the sediment interaction with mat forming root systems of such invasive plants. In the present study, occurrence of extensive macrophyte water hyacinth (*E. crassipes*) growth was evident along downstream stations of the river system

Table 3 C/N variations during different seasons

	PRM	MON	POM
S1	6.12	13.56	9.44
S2	11.53	12.87	10.62
S3	8.27	10.76	14.50
S4	7.35	8.92	7.98
S5	10.16	9.89	11.18
S6	14.61	19.83	12.75
S7	14.85	16.96	14.77

Fig. 6 Field photograph of S6 (railway bridge) station showing macrophytic bloom

especially at S6 (Fig. 6). Sand-Jensen (1998) summarise that macrophytes in Danish eutrophic streams can retain approximately 80% of the sediment transported downstream. However, our result illustrates an average C/N ratio in accordance with values for tropical zones (Tian et al. 2010). Moreover, several studies indicate that substantially high concentrations of nitrogen reported in tropical and subtropical regions were associated with recalcitrant humic materials (Post et al. 1985).

Conclusion

Temporal evaluation of water quality exhibits prominent increase in DOC_{wat} concentrations during PRM, which indicates significant control of tropical summer environment in controlling the organic carbon transport. Comparatively, low values noted during monsoon for most water quality parameters illustrate dilution effect in the river system. Intensification of TP_{sed} toward downstream stretches of the river system is noted during the study. Massive rise in TC_{sed} values exposed along downstream stretches reveals the influence of lithological factors such as recent marine deposits while TN_{sed} values highlight incorporation of humic materials and agricultural runoff, which is evident from correlation values with TP_{sed} during PRM and POM. C/N_{sed} values along downstream stations (S6 and S7) demonstrate

accumulation of terrestrial organic matter and convey the influence of macrophyte in controlling sediment dynamics. Hence, this study recommends two management approaches, viz. (i) timely implementation of Best Agricultural Management Practices (in plantation and agricultural sectors) along with (ii) regular monitoring and removal of macrophytes in downstream stretches of MRB, as a good ecosystem management measure to tackle this issue.

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