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ORIGINAL PAPER

Effect of land use on the biogeochemistry of dissolved nutrients and suspended and sedimentary organic matter in the tropical Kallada River and Ashtamudi estuary, Kerala, India

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Abstract The effect of land use on the biogeochemistry of small tropical rivers and their estuaries was studied using the Kallada River and Ashtamudi estuary located in the State of Kerala, India, as a model system. Water, suspended matter and sediments collected during the monsoon and intermonsoon periods in 2002 and 2003 were analyzed for dissolved nutrients (nitrate, nitrite, phosphate, silicate) and for phytoplankton abundance and composition, amino acid contents and stable carbon (C)) and nitrogen (N) isotope ratios. Seasonal and spatial variations of dissolved nutrients and suspended matter along the course of the river point to distinct differences in the C and N sources that are controlled by hydrology, geology and land use. Unusually low concentrations of dissolved silicate and suspended matter suggest low erosion rates of the Precambrian basement rocks and the firm lateritic soils in non-agricultural areas. Most dissolved nutrients and suspended particulate organic matter originated from fertilized agricultural soils. The biogeochemistry of sedimentary organic matter indicates that most of the Kallada River load is deposited in the upper Ashtamudi estuary, while the middle and lower parts have a stronger marine influence. The spatio-temporal variation of dissolved and particulate river fluxes clearly indicates an effect of land use and land cover on the biogeochemistry of the Kallada River. While the phosphate yield was high (6×10^3 mol km^{-2} year^{-1} or 185 kg km^{-2} year^{-1}), the N yield was relatively low (10×10^3 mol km^{-2} year^{-1} or 141 kg km^{-2} year^{-1}), which is unlike the situation in many other densely populated regions of tropical Asia.

Keywords Amino acids · Biogeochemistry · Land use · Nutrients · Rivers · Stable isotopes

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Introduction

Human activities in coastal zones and contributing watersheds have dramatically changed the fluxes and biogeochemical composition of river inputs into the coastal seas during the so-called ‘Anthropocene’, the period after the Industrial Revolution. At the present time, more than half of the large river systems of the world are affected by dams or other hydrological alterations (Rosenberg et al. 2000; Nilsson et al. 2005). The additional sediment input into the ocean derived from increased soil erosion due to deforestation and land use change has been calculated to 2.3 × 10^9 t $year^{-1}$, while the amount of sediments retained in reservoirs behind dams amounts to 3.7 × 10^9 t $year^{-1}$. The net effect is a reduction of sediment fluxes by 1.4 × 10^9 t $year^{-1}$ to the actual 12.6 × 10^9 t $year^{-1}$ (Syvitski et al. 2005). The riverine nitrogen (N) and phosphorus (P) inputs into the ocean tripled from the 1970s to the 1990s, whereas the input of dissolved silicate almost exclusively stemming from natural sources significantly fell during that same time period. These changes are attributed to changes in land use and land cover and the disposal of industrial and urban wastewater in combination with hydrological alterations (Smith et al. 2003).

Changes in the amount and ratios of the essential nutrients N, P and silicon (Si) have further consequences for the ecology and biogeochemistry of the rivers and receiving coastal water bodies (e.g. Dudgeon 2000; Ittekkot et al. 2000; Rosenberg et al. 2000). Changes in the plankton community structure, toxic algal blooms and hypoxic or anoxic conditions in the water column of coastal seas are examples of the effects of anthropogenically induced environmental changes that have occurred, for example, in the Mississippi River and the Gulf of Mexico. The Mississippi is one of the largest rivers in the world and drains a major portion of the USA. Intensive use of agrochemicals in the Mississippi catchment led to a significant increase in the dissolved N load of the river in the past century. Attendant with an increase in N fertilizer use in the USA—from about 3 × 10^6 t $year^{-1}$ in the 1960s to 12 × 10^6 t $year^{-1}$ in the 1990s—the nitrate concentration of the river increased from about 40 to 120 μM (Goolsby et al. 2000). During this same period, the silicate concentration decreased from 155 to approximately 100 μM. Changes in the nutrient flux and composition has also led to changes in the phytoplankton community structure. As a consequence of massive algal blooms, the decomposition of the very high biomass led to extensive zones (up to 20,000 km^2) of midsummer hypoxia in the Gulf of Mexico (Rabalais et al. 2000). Our knowledge of these processes and quantitative estimates exist mainly from large river catchments in temperate regions, such as in the case of the Mississippi.

Such information is scarce on coastal regions of tropical South and Southeast Asia, which are among the regions most heavily modified by human activities worldwide and are where rivers transport a major part of the annual global input of water, sediment, carbon (C) and nutrients to the ocean. Annually, about 22% of water and 47% of sediment are discharged into the ocean by Asian rivers (Degens et al. 1991; Milliman et al. 1999; Syvitski et al. 2005). A major part of the world population, i.e. 3.6 billion people, live in Asia, and to a large extent they economically depend on the natural resources of coastal regions. More than two thirds of the 45,000 large dams operating in the world are located there, and 81% of the annual water withdrawal is for agriculture (Elvidge et al. 1997; The World Commission on Dams 2000; Smith et al. 2003; Nilsson et al. 2005; World Resources Institute 2005).

The number of dams operated in India is relatively low, whereas 86% of water withdrawal was for agriculture in the year 2000 (The World Commission on Dams 2000; World Resources Institute 2005). Most of the rivers on the western coast of India discharging into the Arabian Sea are small- to medium-sized. For a long time, the fluxes of dissolved and particulate substances from these types of rivers were generally considered to be insignificant for global budgets. However, Milliman and Syvitski (1992) demonstrated that small mountainous rivers contribute more suspended sediment to the annual global load than previously thought. The sheer catchment size of large rivers and the multitude of possible human activities may dampen the effects of individual activities and prolong the response time on these activities. Therefore, small-sized rivers appear to be more suitable for process studies because the response time should be shorter and the effects of individual human activities on water quality and biogeochemistry of the rivers should be more easily identifiable.

Here, we present results from biogeochemical studies on water, suspended matter and sediments from the Kallada River and Ashtamudi Estuary in the southern Indian State of Kerala. The Kallada is a small mountainous river which discharges into the Arabian Sea through an estuarine lagoon, the Ashtamudi. Agriculture and other human activities in the extremely densely populated catchment should leave an distinguishable imprint on the fluxes and composition of dissolved and particulate substances transported by the river. In combination with information on geology, hydrology and land use, we have attempted to delineate the effects of the various natural and anthropogenic control factors on the water quality and biogeochemistry of the river and its estuary.

Materials and methods

Study area

The State of Kerala stretches over 560 km along the coast of the Arabian Sea and is flanked to the east by the Western Ghats mountains. The climate of the region is governed by two different monsoon seasons. Peak rainfall occurs from May to July during the southwest monsoon and from October to mid-December during the northeast one. Available daily precipitation data for the period 1994–2004 indicate a general shift of peak rainfall from June to October when compared to the 149-year average. During the October 2002 period of this investigation, maximum precipitation was almost twofold higher than the 149-year average (Fig. 1).

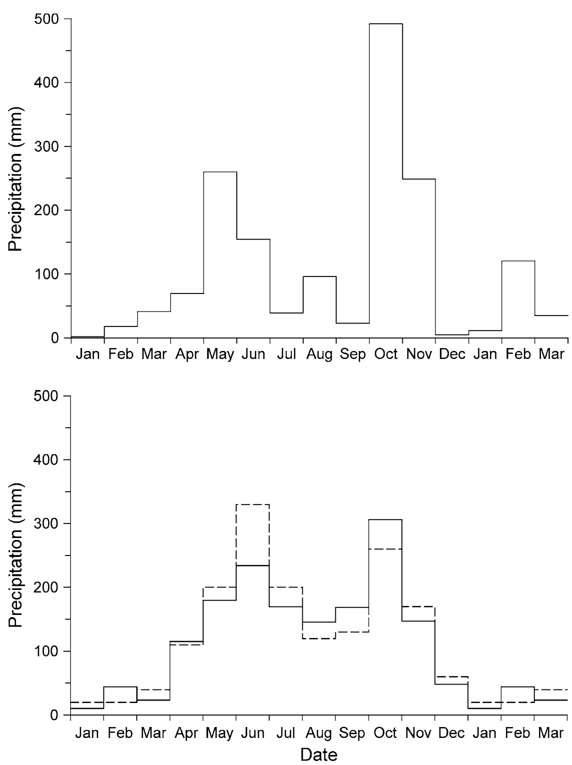

Fig. 1 Monthly average precipitation (mm) at Thiruvananthapuram. **Upper panel** Data from January 2002 to March 2003, **lower panel** *Solid line* Average precipitation during the period 1994–2004, *dashed line* the 149-year average. Data are from the Utah Climate Center (2006) and Weatherbase (2006)

Kerala's population density increased by 9.3% from 1991 to entail a total of 819 inhabitants km^{-2} in 2001 (Office of the Registrar General 2003), which is almost threefold higher than the Indian average (World Resources Institute 2005). Agriculture is a major land use in Kerala. The economic demands of the rapidly growing population and the attendant land use and land cover change affect environmental conditions in river catchments. These, in turn, will likely result in changes in water quality and the nature and quantity of the dissolved and particulate loads of Kerala's 44 rivers discharging into the Arabian Sea, entailing further changes for coastal waters and their natural resources.

Samples were collected from the Kallada River and the Ashtamudi estuary. The Kallada River is a 7th order stream with a catchment area of 1699 km^2. It flows through the Tenmala shear zone and discharges into the Arabian Sea through the Ashtamudi estuary (Fig. 2). The discharge of the Kallada River is highest during June to October, and in the period 1980–1995, there was an annual average discharge of 1.58 km^3 year^{-1}. In 1986, a dam was constructed in the upstream region at Parappar for irrigation purposes. Seasonal discharge patterns of the river before and after damming are distinctly different, as shown in Fig. 3: in the period 1987–1995, the peak discharge shifted to October and November. This peak corresponds well with the changes in precipitation in past decades in which there has been a trend for peak rainfall to occur in October/November. Also, the annual average discharge of the river increased from 1.35 km^3 year^{-1} before damming to 1.85 km^3 year^{-1} after damming. However, it is unlikely that damming increased river discharge. Although the available time-series data do not enable precipitation in that part of Kerala during the years 1980–1995 to be quantified, based on observed global trends, model simulations indicate an increase in precipitation in South Asia for the 21st century and an increase in seasonality, with more pronounced dry seasons and increased precipitation throughout the rest of the year (Christensen et al. 2007). It is therefore conceivable that an increase in precipitation is responsible for the observed increase in the discharge of the Kallada River.

The catchment can be subdivided into four major parts according to land cover and use. The upper catchment consists primarily of natural forest with

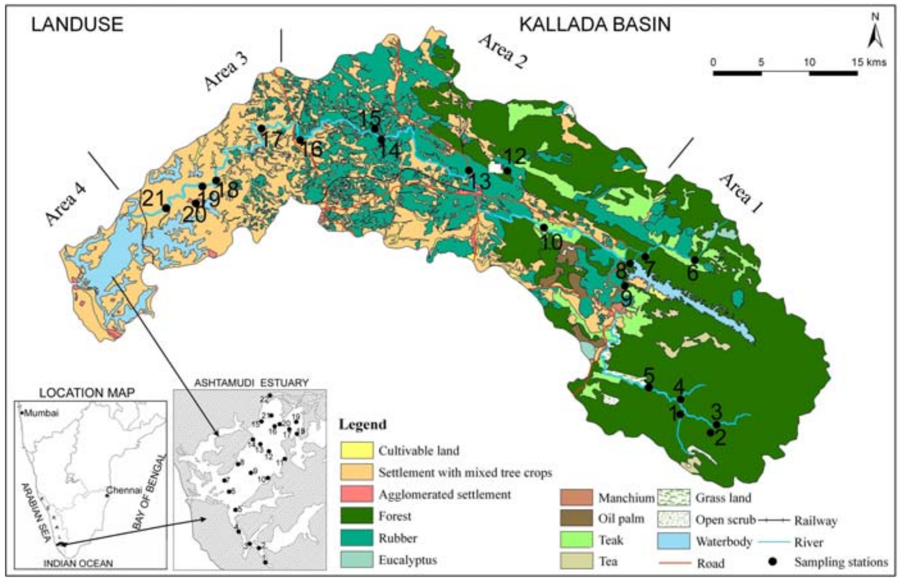

Fig. 2 Map of the investigated area, including land use and stations sampled in the Kallada River and Ashtamudi estuary

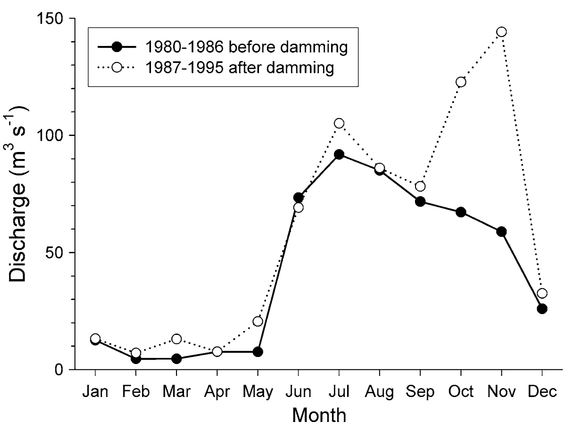

Fig. 3 Average seasonal discharge pattern of the Kallada River. *Bold solid line* Discharge during the period 1980–1986 (before damming), *dotted line* discharge during the period 1987–1995 (after damming)

small patches of teak and tea cultivation (area 1, river km 0–37). It is represented by stations 1–8a and contains the Parappar dam and reservoir. The adjacent part downstream is a mixture of forest and agricultural plantations (area 2, river km 37–63), which is represented by river stations 9–13. The lower part of the catchment is a mixture of settlements with mixed tree crops and patches of rice cultivation and rubber and coconut plantations (area 3, river km 63–121). It is represented by stations 14–21.

The Ashtamudi estuary is the interface between the Kallada River and the Arabian Sea (area 4, sample stations A1–A23). The estuary is connected to the ocean through a small outlet. The Ashtamudi estuary (area 4) can be divided into three geographic sections, the open estuary (stations A5–A14, middle and lower estuary), the Kollam section in the southeast (stations A1–A4, a finger-like branch with reduced exchange of water, surrounded by mangrove and coconut plantations) and the Kallada section in the northeast (stations A15–A23, upper estuary) that forms the transition to the river. During the monsoon season salinity can drop to values <10 in the whole estuarine lagoon and zero near the freshwater sources, mainly the Kallada River. However, during other times of the year, salinity ranges between 30 and 35 in the open estuary; it is considerably lower only in the Kollam section and, in particular, in the transition to the Kallada River (Muraleedharan Nair et al. 2001).

Sampling

The river was sampled for water, total suspended matter (TSM) and phytoplankton in July/August 2002 (southwest monsoon), October 2002 (northeast monsoon) and March 2003 (intermonsoon, dry season). The Ashtamudi estuary was sampled for water, TSM, sediments (upper 2 cm) and phytoplankton in October 2003. Water samples for dissolved nutrients were filtered into plastic bottles and stored at 4°C until analysis, which occurred a maximum of 2 days after sampling. For the collection of TSM, 20- to 40-l water samples were collected in polyethylene tanks. The water was filtered through cellulose nitrate filters (diameter 45 mm, pore size 0.45 μm) and the filters subsequently sun dried. The TSM and sediment were ground and homogenized in an agate mortar and pestle prior to analysis. Phytoplankton samples were obtained by filtering 5 l of surface water (0–0.5 m water depth) through a net (mesh size 35 μm). The material retained in the net was washed in 100-ml polyethylene bottles and the samples preserved in formalin solution.

Analysis

Physicochemical parameters were determined by standard methods (APHA 1985). Salinity is reported in practical salinity units (psu). Water samples were analyzed spectrophotometrically for dissolved nutrients nitrate, nitrite, phosphate and silicate (precision ±0.1 μM; Grasshoff et al. 1999). Total C and total N of the TSM and sediments were determined by high-temperature combustion in a Carlo Erba NA 2100 elemental analyzer (Verardo et al. 1990). Organic carbon (C_{org}) was determined in a similar manner after the removal of carbonate by acidification with 1 *N* HCl and subsequent drying at 40°C. Inorganic C was calculated by subtracting organic from total C. Duplicate analyses resulted in an average relative error of 0.18% for C and 0.07% for N.

Total hydrolyzable amino acids (AA) and total hydrolyzable hexosamines (HA) of the TSM and sediments were analyzed with a Pharmacia LKB (Uppsala, Sweden) Alpha Plus 4151 amino acid analyzer after hydrolysis with 6 *N* HCl for 22 h at 110°C. Hexosamine concentrations were multiplied by a factor of 1.4 to compensate for losses during hydrolysis (Müller et al. 1986). The AA and HA were separated on a cation exchange resin and detected fluorimetrically (Roth and Hampai 1973). A detailed description of the procedure is given by Jennerjahn and Ittekkot (1999).

The N isotope composition ($\delta^{15}N$) of TSM and sediments was determined with a Finnigan (San Jose, CA) Delta Plus gas isotope ratio mass spectrometer after high temperature combustion in a Flash 1112 EA elemental analyzer. The $\delta^{15}N$ is given as ‰—deviation from the N isotope composition of atmospheric N_2. The C isotope composition ($\delta^{13}C_{org}$) was determined in a similar manner following the removal of carbonate by adding 1 *N* HCl and subsequent drying at 40°C. $\delta^{13}C$ is given as ‰—deviation from the C isotope composition of the PDB standard. The standard deviation of replicate measurements was 0.2% for both $\delta^{15}N$ and $\delta^{13}C_{org}$.

Calculation of budgets

Monthly average discharge data of the Kallada River from the period after damming were used for the calculation of budgets. Monthly loads were calculated by multiplying monthly discharges with the concentrations of dissolved and particulate substances and then summing up the monthly loads to calculate annual river loads. Concentrations from October 2002 and March 2003 (August 2002 for TSM) were used for the high (June–November) and low discharge periods (December–May), respectively. Concentrations from stations next to the river mouth were taken for budget calculations (station 21 at river km 121 for nitrate, phosphate, silicate; station 19 at river km 112 for TSM).

Statistics

Statistical analysis was performed with the software PRIMER-6 (Primer-E, Lutton, Ivybridge, UK). Similarity matrices were constructed on normalized data using the Euclidean distance similarity measure. Separate multivariate analysis of similarities (one-way ANOSIM) was performed on data from (1) the Kallada River water to evaluate dissimilarities between months and (2) the Ashtamudi sediments to evaluate dissimilarities between estuary sections. Variables used for Kallada River water were dissolved oxygen (DO), pH, nitrate, phosphate and silicate. Variables used for Ashtamudi sediments were $CaCO_3$, C_{org}, N, $\delta^{13}C_{org}$ and $\delta^{15}N$. The BEST/BIOENV routine (biota and/or environment matching using Spearman rank correlation) was used to determine the factors which best explain the observed dissimilarities. All tests were considered to be statistically significant at p level <0.05.

Results

Physicochemical parameters, dissolved nutrients and phytoplankton in the Kallada River

Physicochemical parameters and dissolved nutrients varied both seasonally and longitudinally along the course of the river. The pH varied only slightly around an average of 6.9 ± 0.2 along the course of the river in July 2002, but it dropped significantly in October 2002 (average pH 5.8 ± 0.2) and then increased to an average of 6.3 ± 0.2 in March 2003. Similarly, DO displayed little spatial variation. From an average of 7.3 ± 0.7 mg l^{-1} in July 2002, DO dropped to 6.6 ± 1.4 mg l^{-1} in October 2002 and finally to 5.5 ± 0.5 mg l^{-1} in March 2003.

Silicate ranged between about 89 and 103 µM in the headwaters (area 1) in July 2002 (Fig. 4). It was about 20 µM lower during October 2002 and then increased to values of up to 146 µM in March 2003. Silicate levels dropped to 50–70 µM in the Parappar reservoir near the dam at river km 37, with no seasonal variations. Downstream of the reservoir, silicate concentrations did not display any statistically significant seasonal or geographical trend. The patterns of dissolved nitrate and dissolved phosphate were different (Fig. 4). Nitrite levels were always <1 µM. In contrast, nitrate levels ranged from 2.6 to 11.7 µM in July 2002 and increased downstream, while in October 2002 they ranged from 3.6 to 27.6 µM. Although nitrate concentrations did not display a statistically significant trend, maximum nitrate occurred in area 3 between river km 70 and 90, except for the absolute maximum in the reservoir lake. Nitrate concentrations were generally lower but displayed a downstream increase in March 2003, particularly in area 3, and then dropped again at the entrance to the Ashtamudi estuary. Phosphate levels ranged from 1.0 to 1.7 µM in July 2002 and from 0.7 to 2.2 µM in March 2003 and displayed little variability along the course of the river. In October 2002, however, the phosphate level was fourfold higher and increased from the source towards the Ashtamudi estuary (Fig. 4). Statistical evaluation of the data sets on physicochemical parameters and dissolved nutrients revealed a significant difference ($p = 0.001$ each) between the three investigated periods (ANOSIM: complete set $R = 0.612$; pairwise tests: July/October $R = 0.710$, July/March $R = 0.579$, October/March $R = 0.569$). Differences between July and October were best explained by pH alone (BEST: $\rho = 0.835$, $p = 0.001$) or by pH and phosphate in combination (BEST: $\rho = 0.817$). Differences between July and March were best explained by pH and DO in combination ($\rho = 0.679$, $p = 0.001$), and differences between October and March by phosphate alone ($\rho = 0.699$, $p = 0.001$), but almost as well by phosphate in combination with pH ($\rho = 0.664$).

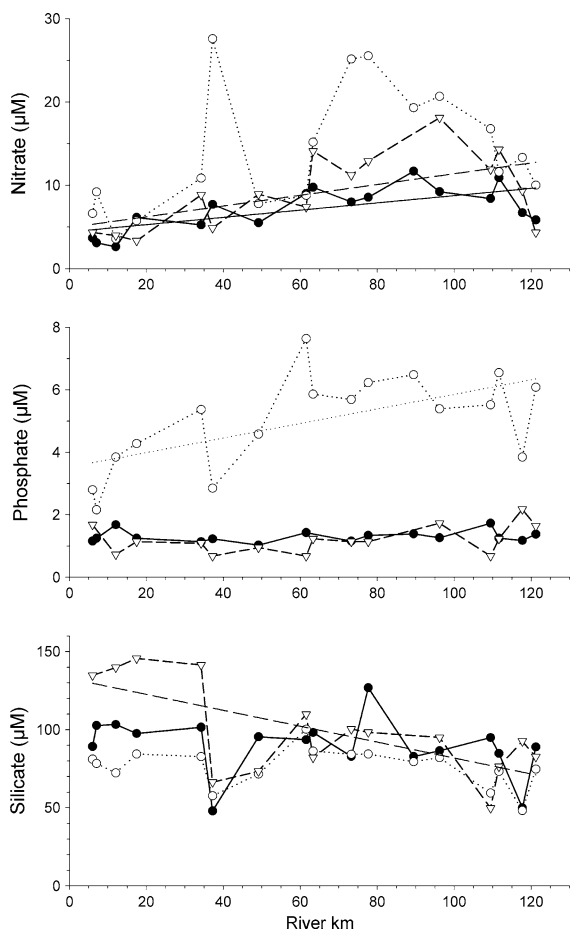

Fig. 4 Concentration of nitrate (upper panel), phosphate (middle panel) and silicate (lower panel) along the course of the river during July 2002 (*filled circles*, *solid line*), October 2002 (*open circles*, *dotted line*) and March 2003 (*triangles*, *dashed line*). *X-axis* River kilometers, with increasing distance from the spring (km 0). Linear regressions ($p < 0.01$, $n = 17$): nitrate July 2002 $Y = 0.04X + 4.42$, $R^2 = 0.44$; nitrate March 2003 $Y = 0.06X + 4.94$, $R^2 = 0.32$; phosphate October 2002 $Y = 0.02X + 3.53$, $R^2 = 0.38$; silicate March 2003 $Y = -0.51X + 132.8$, $R^2 = 0.46$

Phytoplankton abundance was generally low. Concentrations were <1000 cells l^{-1} in October 2002, with the exception of stations 8 (Parappar reservoir near dam, river km 37) and 21 (near river mouth, river km 121). The concentrations were still low during the period of low rainfall in March 2003, but higher than in October 2002. Peak abundance of >13,000 cells l^{-1} was observed at station 8 near the Parappar dam (Fig. 5). Phytoplankton was composed of Chlorophyceae (66%), Bacillariophyceae (23%), Cyanophyceae (11%) and Dinophyceae (<1%) and displayed little seasonal variation.

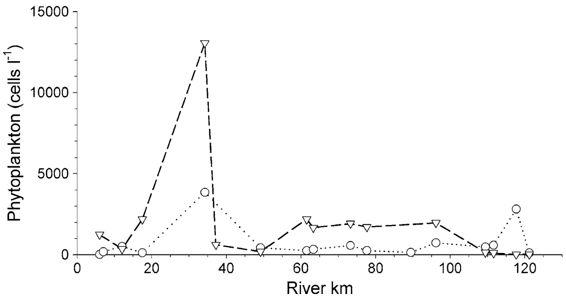

Fig. 5 Phytoplankton cell counts along the course of the river during October 2002 (*open circles*, *dotted line*) and March 2003 (*triangles*, *dashed line*)

Total suspended material and its biogeochemical composition in the Kallada River

The TSM content of the Kallada River was generally low when compared to that of other rivers of South and Southeast Asia (Tables 1 and 2). It increased from a very low concentration of 3.3 mg l^{-1} in the forested headwaters downstream to 42.4 mg l^{-1} at station 17 (river km 96), and increased by three- to fourfold from August, with only 96 mm of rainfall, until October, with 492 mm of rainfall. Similarly, from August to October, C_{org} and N concentrations increased, while the C_{org} percentage remained almost constant and the N percentage decreased from August to October. This resulted in a C/N ratio between 7.1 and 12.7, with lower values during August and an increase towards October 2002.

The AA and HA concentrations in TSM varied from 10.0 to 21.3 mg g^{-1} and from 1.6 to 3.5 mg g^{-1}, respectively. Maximum concentrations were found in forested area 1 and decreased downstream. In contrast, the portion of C accounted for by AA (AA-C%) increased from minimum values of 11.7% in area 1 to 19.8% in area 3 downstream. The portion of N accounted for by AA (AA-N%) increased from a minimum of 30.3% in area 1 downstream to a maximum of 67.1% in area 3 and, in contrast to AA and AA-C%, displayed an increase on the order of 10–20% from August to October 2002. The reactivity index RI varied between 1.4 and 1.7 in area 3 and was higher in area 1 (Table 2). The RI is the ratio of the aromatic (tyrosine and phenylalanine) and the non-protein AA (β-alanine, γ-aminobutyric acid). Fresh organic material (OM) contains higher portions of aromatic AA, while the non-protein AA are metabolic products of aspartic acid and glutamic acid (Lee and Cronin 1982; Jennerjahn and Ittekkot 1997). The RI is used as a sensitive indicator of OM diagenesis, the lower the values the stronger degraded is the OM (Jennerjahn and Ittekkot 1997; Suthhof et al. 2000).

A minimum $\delta^{13}C_{org}$ of −26.9‰ and the least seasonal variation was observed in forested area 1, thereby falling in the typical range of C3 plants (e.g. Lacerda et al. 1986; Jennerjahn et al. 2004). Downstream $\delta^{13}C_{org}$ values displayed seasonal variation on the order of about 2‰. $\delta^{15}N$ displayed both seasonal and spatial variability, increasing from −2.7‰ in the forest to 5.4‰ downstream and by a twofold from August to October (Table 1).

Physicochemical parameters, dissolved nutrients, phytoplankton and sediment biogeochemistry in the Ashtamudi estuary

During the time of sampling in October 2003 the Ashtamudi estuary was characterized by brackish to marine conditions, as indicated by salinity and pH, the latter of which ranged between 8.1 and 8.4. Salinity displayed a minimum of 18.0 at station A22 where the Kallada enters the estuary, ranging between 20.3 and 24.8 at stations A1–A3 in the Kollam section and between 26.1 and 28.5 in the rest of the estuary. The DO ranged between 3.0 and 7.1 mg l^{-1}, with minimum values occurring in the Kollam section. Nitrate varied between 4.4 and 26.1 µM. Phosphate decreased from 3.3 µM at station A1 to 1.2 µM at station A4 and varied between 0.1 and 0.8 µM throughout the rest of the estuary. Nitrate and phosphate levels as well as the N/P ratio, which ranged from 3.8 to 67.1, did not display any trend with salinity. Silicate had a maximum of 64.2 µM at station A22 where the Kallada enters the estuary; throughout the rest of the estuary, it ranged between 36.4 and 49.1 µM without displaying any trend with salinity.

Phytoplankton abundance increased from 47 cells l^{-1} near the river mouth to 121 × 10^3 cells l^{-1} near the sea (Table 3). Phytoplankton composition displayed little spatial variation. Bacillariophyceae were the dominant group, making up 68% of the phytoplankton community on average, while Chlorophyceae, Cyanophyceae and Dinophyceae contributed 13, 10 and 5%, respectively. Most of the observed 43 diatom species were marine forms, with the major species being *Chaetoceros indicus*, *Skeletonema costatum* and *Chaetoceros lorenzianus.*

Table 1 Concentration and biogeochemical properties of TSM from the Kallada River in area 1 (St. 5) and area 3 (St. 17 and 19) in August and October 2002 and from fertilizers, plants and soils from the Kallada River catchment

Study locations/areas	TSM (mg l^{-1})	C_{org} (%)	N (%)	C/N	$\delta^{13}C_{org}$ (‰)	$\delta^{15}N$ (‰)	Reference[a]
Kallada River TSM							
St.5, Aug. 2002	3.3	7.8	1.0	7.9	−26.6	−2.7	1
St.5, Oct. 2002	13.3	7.9	0.7	10.9	−26.9	−1.3	1
St.17, Aug. 2002	18.7	2.9	0.4	8.3	−25.1	1.9	1
St.17, Oct. 2002	42.4	3.2	0.3	12.7	−26.9	2.3	1
St.19, Aug. 2002	10.2	3.9	0.6	7.1	−26.0	2.3	1
St.19, Oct. 2002	31.7	2.7	0.2	11.6	−24.2	5.4	1
Kallada catchment fertilizers							
Organic manure		34.3	2.0	17.2	−19.9	6.6	2
Fresh cow dung		28.0	1.6	17.5	−20.4	7.0	2
N:P (18:18)		2.6	7.7	0.3	−27.1	2.8	2
N:P:K (10:10:4)		3.3	5.5	0.6	−27.2	−0.9	2
Kallada catchment crop plants							
Area 2, green rubber leaf		51.1	3.1	16.5	−30.7	4.3	2
Area 2, dry rubber leaf		48.7	1.3	37.5	−29.2	3.7	2
Area 2, green banana leaf		43.4	2.2	19.7	−25.7	9.7	2
Area 2, green coconut leaf		49.5	1.3	38.1	−31.4	4.5	2
Kallada catchment soils							
Area 1, alluvial deposit		4.0	0.2	17.2	−28.4	2.8	2
Area 1, brown soil near St. 5		1.6	0.1	20.5	−20.2	6.4	2
Area 1, red soil (subsurface) near St. 5		0.5	<0.1	15.0	−22.8	6.2	2
Area 2, topsoil near St. 9		0.4	<0.1	12.0	−22.6	6.3	2
Area 2, rubber plantation, near St. 10		2.0	0.1	17.9	−24.2	7.8	2
Area 3, near St. 17		1.1	0.1	21.0	−25.1	5.0	2

TSM, Total suspended material; St., station

[a] Data sources: 1, this paper; 2, Henkel (2006)

In Ashtamudi sediments, C_{org} varied between 0.3 and 3.5% and N between <0.1 and 0.3%. The C/N ratio ranged between 9.7 and 17.7. $\delta^{13}C_{org}$ varied between −25.9‰ and −20.2‰ and $\delta^{15}N$ between 4.7‰ and 8.3‰ (Table 3). Statistical evaluation of the data set on the biogeochemical composition of sediments revealed that the difference between the three sections was significant (ANOSIM: $R = 0.489$, $p = 0.001$), with the major part caused by $\delta^{13}C_{org}$ and $\delta^{15}N$ (BEST: $\rho = 0.628$, $p = 0.001$).

Nutrient and TSM budgets of the Kallada River

Calculation of nutrient budgets resulted in annual loads of 17.1×10^6 mol or 239.0 t for nitrate-N, 10.1 $\times 10^6$ mol or 313.7 t for phosphate-P and 140.0×10^6 mol or 3,919.5 t for dissolved silicon; the respective yields were 10.0×10^3 mol km^{-2} year^{-1} or 140.7 kg km^{-2} year^{-1} for nitrate-N, 6.0×10^3 mol km^{-2} year^{-1} or 184.6 kg km^{-2} year^{-1} for phosphate-P and 82.4×10^3 mol km^{-2} year^{-1} or 2,306.9 kg km^{-2} year^{-1} for dissolved Si. The TSM load and yield amounted to 53.0×10^3 t year^{-1} and 31.2 t km^{-2} year^{-1}, respectively.

Discussion

Seasonal variation and sources of dissolved nutrients

The statistically significant seasonal differences in physicochemical and biogeochemical properties of Kallada River water are probably the result of a seasonally varying interaction of natural (hydrology,

Table 2 Amino acid (AA) content and composition of TSM from the Kallada River, TSM and soils from the Indonesian Brantas River and TSM from major world rivers

Study locations/areas	TSM (mg l^{-1})	AA (mg g^{-1})	AA-C% (%)	AA-N% (%)	AA acidic (mole-%)	AA basic (mole-%)	AA neutral (mole-%)	AA S-containing (mole-%)	AA aromatic (mole-%)	AA non-protein (mole-%)	RI
Kallada River TSM											
St.5. Aug. 2002	3.2	21.1	11.7	30.3	22.7	11.2	61.1	0.1	3.3	1.3	2.5
St.5. Oct. 2002	13.3	21.3	11.7	41.6	24.6	10.8	58.8	0.2	3.7	1.7	2.1
St.17. Aug. 2002	18.6	10.0	14.7	40.1	26.0	10.9	57.5	0.2	3.2	2.1	1.5
St.17. Oct. 2002	42.5	11.1	14.7	59.8	32.7	8.7	52.6	0.1	3.2	2.3	1.4
St.19. Aug. 2002	10.2	18.0	19.8	46.2	26.0	12.0	56.2	0.1	3.3	2.0	1.7
St.19. Oct. 2002	31.6	11.1	17.9	67.1	25.0	10.5	58.5	0.1	3.4	2.3	1.5
Brantas River dry season											
Estuarine TSM	30.7	39.7	25.9	91.8	25.0	11.3	56.6	0.4	6.1	0.5	15.1
Reservoir TSM	9.0	229.3	34.1	86.8	23.3	10.4	59.2	0.3	6.7	0.3	30.1
Estuarine sediments		2.6	11.2	66.8	28.4	9.0	55.2	0.8	4.7	1.7	2.9
Reservoir sediments		7.2	35.0	100.0	29.8	9.4	53.9	1.2	3.9	1.7	2.3
Brantas catchment soils											
Freshly planted rice field		5.3	22.5	79.7	25.4	8.9	59.4	0.9	4.4	0.9	5.0
Harvested rice field		0.8	3.0	23.4	29.1	9.0	56.1	0.1	3.7	2.0	1.8
Mature sugar cane field		2.6	8.3	51.2	31.2	9.6	53.5	0.5	2.6	2.4	1.1
Major world rivers TSM											
Mackenzie	140–360	0.8–3.2		24.8–34.5	17.2	27.0	50.4	1.6	3.4	0.4	8.5
St. Lawrence	6–9	8.2–18.7		26.4–28.7	17.8	27.0	48.9	1.5	4.6	0.2	23.0
Magdalena	40–60	6.6–10.3		26.5–59.2	21.3	28.5	44.1	1.3	5.0	0.4	12.5
Orinoco	14–169	0.9–64.2		25.8–63.5	18.4	30.1	44.3	2.0	3.9	0.8	4.9
Parana	10–121	1.0–164.9		33.5–96.9	21.2	23.5	36.6	2.4	5.1	1.2	4.3
Orange	96–102	2.4–3.5		12.5–20.8	18.1	28.8	40.2	1.7	3.7	0.7	5.3
Indus	25–2,044	0.1–80.4		3.1–63.0	24.0	11.4	55.1	1.7	5.1	0.7	7.3
Ganges	9–1,250	<0.1–266.1		15.8–82.0	25.2	14.7	54.2	1.3	5.5	0.8	6.9
Brahmaputra	48–716	0.1–24.2		9.0–86.0	24.2	11.4	52.6	3.0	5.7	1.4	4.1
Mekong				21.0	20.5	16.9	52.3	2.6	6.6	–	–
Changjiang	960–1,240	1.7–13.2		26.2–40.9	21.0	28.8	40.2	1.8	4.5	0.6	7.5
Huanghe	7,860–13,400	0.7–1.7		17.2–22.7	28.2	8.6	53.7	–	3.3	5.9	0.6

Data for Brantas River and major world rivers are from Jennerjahn et al. (2004) and Ittekkot and Zhang (1989)

AA-C%, Portion of carbon accounted for by amino acids; AA-N%, portion of nitrogen accounted by amino acids; RI, Reactivity index (ratio of the aromatic (tyrosine and phenylalanine) and the non-protein amino acids (β-alanine, γ-aminobutyric acid)

Table 3 Average abundance and composition of phytoplankton and biogeochemical properties of sediments from the various sections of the Ashtamudi estuary in October 2003

	Kollam section	Open estuary	Kallada section
Phytoplankton			
Plankton (cells l^{-1})	60,846 (16,138–121,889)	124,002 (3,222–65,935)	3,217 (47–7,636)
Bacillariophyceae (%)	71.9 (46.4–82.8)	90.6 (61.8–98.8)	96.1 (91.5–99.4)
Dinophyceae (%)	0.5 (0.1–1.2)	9.4 (1.2–23.3)	8.6 (1.5–45.4)
Cyanophyceae (%)	27.6 (17.0–52.4)	1.9 (0–9.3)	0.4 (0–1.4)
Chlorophyceae (%)	0	0.6 (0–5.6)	0
Sediments			
C_{org} (%)	2.9 (2.6–3.5)	2.0 (0.7–2.5)	2.0 (0.3–2.8)
N (%)	0.2 (0.2–0.3)	0.2 (0.1–0.2)	0.2 (<0.1–0.2)
C/N	12.8 (10.9–16.3)	10.8 (9.7–12.5)	13.1 (10.7–17.7)
$\delta^{13}C_{org}$ (‰)	−23.6 (−25.9–−22.1)	−20.9 (−21.7–−20.2)	−24.3 (−25.9–−22.7)
$\delta^{15}N$ (‰)	7.0 (6.8–7.4)	6.6 (6.3–8.3)	5.3 (4.7–5.8)

Numbers in parenthesis denote range of values

geology, soils) and anthropogenic (land use) control factors which will be discussed in the following sections.

The silicate concentrations were low when compared to those found in other tropical rivers and, in particular, to those of Asia. On a global scale, wet tropical Asia is among the regions with the highest observed silicate weathering rates (Gaillardet et al. 1999; Jennerjahn et al. 2006). In these so-called transport-limited regimes, weathering rates are so high that river loads are limited by the availability of water rather than by weathering despite abundant rainfall (Drever 1997). The most important factors for the high weathering rates and, consequently, the high riverine silicate load in tropical Asia, are the relatively young geology, active tectonism, steep gradients and high precipitation, high runoff and high runoff temperature (Jennerjahn et al. 2006). In the case of the Kallada River, the dense vegetation cover in the upstream region, the Precambrian basement rocks (Soman 1999) and a low gradient in combination with the firm lateritic soils in the mid- and lowlands are probably responsible for lower weathering and erosion and, hence, the lower level of silicate in the river relative to that found in other rivers of tropical Asia.

In general, nitrate was fairly low when compared to that found in other regions dominated by agriculture (e.g. Turner and Rabalais 1991; Filoso et al. 2003; Voss et al. 2006). For example, in the nearby Chalakudy River, a small tributary of the Periyar River, maximum nitrate concentrations were 99 µM in a region with rice cultivation and 297 µM in urban settlement regions (Chattopadhyay et al. 2005). Near the mouth of the Brantas River in eastern Java, Indonesia, nitrate concentrations were as high as 119 µM. The Brantas River catchment has a population density >1000 inhabitants km^{-2}, and about half of the land use is agriculture (Jennerjahn et al. 2004). The Kallada catchment also has an extremely high population density of >1000 inhabitants km^{-2}, and almost half of the land use is agriculture with fertilizer application. Artificial fertilizers and organic manure are usually applied shortly after the peak monsoon in June/July. Urea is of importance in area 3 where rice cultivation is a major land use. However, when compared to the average of all India (97 kg ha^{-1}) and to other regions of the world (world 91 kg ha^{-1}, Asia 144 kg ha^{-1}, Europe 73 kg ha^{-1}, North America 93 kg ha^{-1}; World Resources Institute 2005; Government of India 2006), fertilizer use is relatively low in Kerala. A P deficiency of the acidic laterite soils requires increased application of P fertilizers (Raychaudhuri 1980). Average fertilizer use in Kerala was 69 kg ha^{-1} in 2002–2003, 29 kg and 14 kg of which were N and P, respectively (Chattopadhyay et al. 2005). The resulting molar N/P ratio of the fertilizer, 4.6, is close to the observed average N/P ratio of 2.9 in Kallada river water in October 2002. Manure, which is also an important organic fertilizer in Kerala, typically has a low N/P ratio (Eghball 2002). Average N/P ratios of 2.6 for feedlot manure and 1.9 for composted manure have been observed in a long-term study in Germany

(Eghball et al. 1997). In the Chalakudy River, average N/P ratios of dissolved nutrients were <5 in forest areas, 5–10 in settlement areas with mixed tree crops and >10 in urban settlement areas, with the highest ratios occurring during times of high rainfall and high river discharge (Chattopadhyay et al. 2005). In many rivers with multiple human impacts, particularly in Europe, the N/P ratio is higher by one or sometimes even two orders of magnitude, mainly due to much higher nitrate concentrations (Table 4; Meybeck 1993; Global Environmental Monitoring System 2000).

The change in land use from native vegetation to agricultural crops may change the stoichiometry of runoff from a region not only through a change in the supply of nutrients, but also by the nutrient requirements of plants and type of agricultural land use (e.g. Arbuckle and Downing 2001; Alexander et al. 2008). The analysis of a global data set of 1280 plant species revealed leaf N and P patterns that are related to temperature and latitude. The leaf N/P ratio increases with increasing temperature and decreasing latitude (Reich and Oleksyn 2004). Although there is a high variability, average leaf N/P ratios of plants from

Table 4 Dissolved nutrients and respective atomic ratios in the Indian Kallada and Chalakudy rivers, world rivers under heavy human impact and world rivers under little human impact

Study locations/areas	Nitrate (μM)	Phosphate (μM)	Silicate (μM)	N/P	Reference[a]
Kallada River					
July 2002	7.2	1.3	96	5.5	1
October 2002	13.4	5.0	78	2.9	1
March 2003	9.6	1.3	102	8.0	1
Chalakudy River					
Forest	30.0	7.7		3.9	2
Plantation	32.9	9.7		3.4	2
Settlement/tree crop	55.0	10.0		5.5	2
Urban settlement	269.3	28.1		9.6	2
Paddy cultivation	66.4	7.1		9.4	2
World rivers under heavy human impact					
Brahmaputra (Bangladesh)	58.6	1.9	130	31.2	3
Ganges (Bangladesh)	61.4	2.3	128	26.2	3
Mississippi (USA)	75.7	6.3	127	12.1	3
Changjiang (China)	55.0	0.4	232	125.7	3
Huanghe (China)	12.1	0.5	128	24.3	3
Ebro (Spain)	107.1	1.2	177	92.7	3
Elbe (Germany)	214.3	11.9	67	18.0	3
Po (Italy)	100.0	2.6	67	38.1	3
Rhine (Germany)	277.1	12.5	87	22.2	3
Weser (Germany)	353.6	17.8	67	19.8	3
Paraiba do Sul (Brazil)	19.8	1.0	110	19.2	4
Brantas (Indonesia)	110.0	2.5	180	44.0	5
World rivers under little human impact					
Amazon (Brazil)	12.1	0.6	115	19.4	3
Tocantins (Brazil)	1.1	0.1		11.4	3
Mackenzie (Canada)	10.0	1.3	50	8.0	3
Lena (Russia)	6.4	0.3	97	20.6	3
Contas (Brazil)	1.6	1.0	75	1.6	6
Mahaweli (Sri Lanka)	5.0	1.1	77	4.5	7
Kidogoweni (Kenya)	0.4	1.7	429	0.2	8
Mkurumuji (Kenya)	17.0	1.3	279	13.1	8

Data from the Kallada River are average concentrations over the entire length of the river for the individual sampling campaigns. Data from the Chalakudy River are annual averages for the various sections of the river catchment according to the major land use

[a] Data sources: 1, this paper; 2, Chattopadhyay et al. (2005); 3, Global Environmental Monitoring System (2000); 4, Carneiro (1998); 5-Jennerjahn et al. (2004); 6, Jennerjahn et al. (2006); 7, Silva et al. (2005); 8, Mwashote and Jumba (2002)

tropical regions are in the range of 10–20. Crop plants have much lower N/P ratios, as indicated by the results of the statistical evaluation of a large database. For example, cereal, grain legume and oilseed species have average N/P ratios of 5.6, 8.7 and 4.5, respectively (Sadras 2006). It would appear that the N/P ratio of the inorganic and organic fertilizers applied in Kerala is lower than the requirements of crops and other plants. It is therefore conceivable that N is efficiently consumed while part of the fertilizer-P can not be taken up by plants. Moreover, the firm texture of the prevailing laterite soils may also hinder the percolation of surface water into deeper soil layers. Consequently, it is likely that surface water runoff and outwashing of soils during times of peak rainfall were responsible for the very high phosphate concentration and significantly lowered pH of river water in October 2002 as well as a generally low N/P ratio during the tilling period.

Seasonal variations in the biogeochemical composition of TSM and its sources

The fairly high percentage of C_{org} and N indicates that the peak monsoon rain in October washed organic-rich soils into the river; these soils probably mainly originated from agriculture. This result is similar to findings from dry (January/February) and wet (August) seasons in the Kallada River in 1997 (Wittkuhn 1999): the TSM concentration was slightly lower in 1997, but the particulate organic carbon (POC) concentration and C/N ratio were similar to our results. Both TSM and POC displayed a threefold increase from the dry to the wet season in our study. These characteristics held true for other rivers in Kerala in 1997 (Wittkuhn 1999). The outwashing of organic-rich soils and the generally low TSM may be due to the Precambrian basement rocks and the firm lateritic soils allowing for less erosion and hence less dilution with mineral matter than observed in other Asian river catchments.

Both AA and AA-C% were lower in our study than in TSM from the Brantas River and coastal waters of Madura Strait in Java, Indonesia, and other tropical rivers (Table 2; Ittekkot and Zhang 1989; Jennerjahn et al. 2004). This and the generally low reactivity index of OM (RI = 1.4–2.5) when compared to TSM from the Brantas River and other coastal regions (Jennerjahn and Ittekkot 1997; Jennerjahn et al. 2004) indicate that the OM has undergone substantial degradation. In the Indonesian Brantas River, catchment soil from a freshly planted rice field had a $\delta^{13}C_{org}$ of −26.0‰, whereas the soil of a harvested field had a $\delta^{13}C_{org}$ of −23.4‰ (Jennerjahn et al. 2004). Stations 17 (river km 96) and 19 (river km 112) in area 3 of the Kallada catchment are located in a mosaic of settlements and rice fields. It is therefore conceivable that the seasonal isotopic variation of river TSM results from a seasonally varying contribution of OM from agricultural soils.

The N isotope composition may be affected by various processes, such as nitrification/denitrification, fractionation during plankton/plant uptake, OM diagenesis or material inputs from different sources (e.g. Wada and Hattori 1990; Schäfer and Ittekkot 1993; Högberg 1997; Holmes et al. 1998; Ostrom et al. 1998; Voss et al. 2001; Stewart et al. 2002; Sebilo et al. 2003; Providoli et al. 2005). High inputs of atmospheric N through N fixation and fractionation during uptake may lead to a low $\delta^{15}N$. Degradation of OM leads to an enrichment of ^{15}N, hence a high $\delta^{15}N$. The $\delta^{15}N$ of Kallada TSM displayed distinct trends with AA composition and reactivity: it increased with decreasing N and AA concentrations and RI and increasing AA-N% (Fig. 6). Both N and AA were high in the forested area 1 and the low $\delta^{15}N$ indicates a predominantly atmospheric N source (N fixation; see, for example, Wada and Hattori 1990). While the maximum RI in area 1 indicates the relative freshness of the OM (Jennerjahn and Ittekkot 1997), a decreasing RI and increasing $\delta^{15}N$ indicate an increasing degree of OM degradation downstream. Moreover, a slight RI decrease in conjunction with a $\delta^{15}N$ increase suggest a higher contribution of degraded OM in October than in August 2002.

Interestingly, $\delta^{15}N$ increased with increasing AA-N% and decreasing RI from August to October 2002 (Fig. 6). Assuming that AA are the labile part of OM that is preferentially degraded compared to bulk OM, one should expect a decrease in AA-N% with increasing $\delta^{15}N$ and decreasing RI, as observed in studies from coastal and marine environments (e.g. Jennerjahn and Ittekkot 1999; Jennerjahn et al. 1999; Suthhof et al. 2000). We observed a different pattern that suggests substantial differences in the soil N pools in the natural forested area 1 and those in downstream lateritic and agricultural soils. The C_{org} and N concentrations and the C/N ratio of TSM in forested

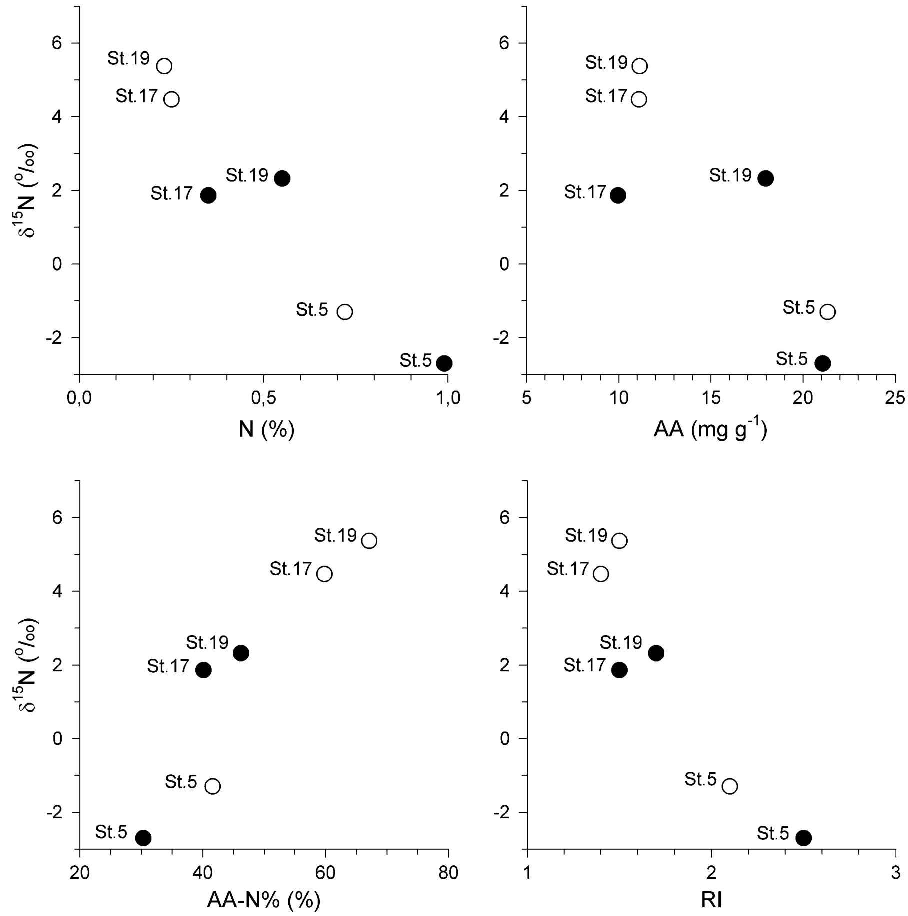

Fig. 6 δ^{15}N of total suspended material from the Kallada River plotted against nitrogen (*N*, upper left panel), amino acids (*AA*, upper right panel), portion of N accounted for by amino acids (*AA-N%*, lower left panel) and reactivity index (*RI*, lower right panel) for August 2002 (*filled circles*) and October 2002 (*open circles*). *Numbers in plots* denote stations along the river

area 1 were in the range of those found in soils of natural and secondary forests of a north-eastern Himalayan region of India under a subtropical monsoon climate (Arunachalam et al. 1999). While the C/N ratio displayed little variation, the C_{org} and N concentrations of downstream TSM were much lower than in the above-mentioned soils.

The relative contribution of acidic AA in Kallada TSM increased at all stations from August to October 2002 and was in the range of TSM from the Indus, Ganges and Brahmaputra rivers but higher than that found in TSM from other major world rivers. It was also in the range of that found in estuarine sediments and agricultural soils from the Brantas River catchment (Table 2) where about 50% of the land use is agriculture, two thirds of which are irrigated rice under fertilization. The major part of its high sediment load during the wet season is deposited in the prograding delta of the Porong, the major branch of the Brantas River discharging into coastal waters of Madura Strait. Amino acid composition and stable isotope data of estuarine/deltaic sediments indicate a high contribution of OM derived from agricultural soils (Jennerjahn et al. 2004). Investigations on the composition of N in soils have shown that the portions of basic AA in N-depleted soils from the arctic and cool temperate climate zones are higher than those in soils from tropical climates with a higher N content. Enrichment of basic AA in high latitude soils is thought to be a consequence of long residence times and leaching that preferentially removes soluble OM compounds (Sowden et al. 1977; Ittekkot and Zhang 1989). This probably does not hold true for the wet tropics where precipitation and runoff are generally much higher. As a consequence of the fast erosion, the residence time of soils and, consequently, also the time for leaching of soluble compounds from the soils is much shorter, not allowing for enrichment of basic AA.

Fertilizer application in agriculture may affect the δ^{15}N of Kallada TSM. Industrial fertilizer produced by the chemical fixation of atmospheric N_2 has a δ^{15}N close to 0‰, while organic fertilizers that have undergone several steps of metabolic alteration are enriched in ^{15}N. For example, in a study from temperate Korea, Choi et al. (2003) investigated the N isotope composition of inorganic and organic fertilizers and plants and soils under fertilization. The δ^{15}N of artificial inorganic fertilizers ranged between −3.9‰ and 0.5‰, while those of organic composts ranged between 15.4‰ and 19.4‰. Soils with inorganic fertilizer applied had a δ^{15}N of 5.9 ± 0.7‰, and those fertilized with compost had a δ^{15}N of 8.8 ± 2.0‰. Crop plants from the investigated area displayed a larger difference, with δ^{15}N values of 4.1 ± 1.7‰ (inorganic fertilizer applied) and 14.6 ± 3.3‰ (compost applied). Although other transformation processes in soils also affect N cycling (e.g. Högberg 1997), the results of Choi et al. (2003) suggest that the application of inorganic versus organic fertilizers leaves a distinguishable imprint on the δ^{15}N of the respective plants and soils.

Fertilizer application is negligible in forested area 1 of the Kallada catchment. The low δ^{15}N of river TSM there appears to be caused by a high portion of N fixed from the atmosphere by vegetation and associated microbes. Negative values are probably due to discrimination against ^{15}N during biological uptake (e.g. Wada and Hattori 1990). While the $\delta^{13}C_{org}$ of TSM falls in the range of soils from the area, the δ^{15}N of TSM in area 1 was much lower than that of soils (Table 1; Henkel 2006). The slightly higher δ^{15}N and lower RI of TSM during the period of high rainfall in October 2002 may have been caused by a larger portion of more degraded soil OM. In area 3, the δ^{15}N of river TSM was around 2‰ in August 2002, shortly after the sowing and fertilizing period. This value falls in the range of the δ^{15}N of artificial fertilizers and crop plants in the Kallada catchment (Table 1; Henkel 2006). The δ^{15}N of river TSM increased to around 5‰ in October 2002. The isotopic composition of TSM during that time was close to that of soil from area 3, indicating that the major part of the TSM originated from the soils.

Leaching is an important component of the weathering process that removes silica and nutrients during wet periods. However, exposure during dry periods may harden the soil and make it less prone to erosion (Raychaudhuri 1980). In contrast, tilling loosens the soil, making it more susceptible to erosion. Therefore, the low δ^{15}N of river TSM in area 3 in August 2002 suggests that the majority of the generally low river POC during that time originated from freshly fertilized agricultural soils. Low N concentrations in river TSM were probably due to dilution with mineral matter during torrential rainfalls in October 2002. Most of this N appears to originate from agricultural soils, as indicated by the isotopic composition, the high AA-N% and the enrichment of acidic AA (Table 2; Fig. 6). Discrimination against ^{15}N during the mineralization–plant uptake process (Högberg 1997) may have lead to an enrichment of ^{15}N in the agricultural soils from the sowing/fertilizing period until the peak rainy season, resulting in the observed shift in river TSM from August to October 2002.

Sources and transformation of OM deposited in the Ashtamudi estuary

Average sedimentary C_{org} concentrations of 2.0% in the open estuary and the Kallada section were lower than in the Kollam section, but they were still considerably higher than those found in the Indonesian Brantas River estuary and on other tropical shelves (Westerhausen et al. 1993; Jennerjahn and Ittekkot 1997; Suthhof et al. 2000; Jennerjahn et al. 2004). Dual stable isotope plots of samples from the three different sections of the Ashtamudi estuary point to differences in sources and diagenesis of OM (Fig. 7). Sediments from the open estuary had the highest $\delta^{13}C_{org}$ values, which is consistent with the range of $\delta^{13}C_{org}$ values for marine phytoplankton from tropical regions (e.g. Fischer 1991; Matsuura and Wada 1994) and distinctly different from those of the Kollam and Kallada sections. This and the phytoplankton dominance by marine diatom species indicate the predominantly marine origin of C deposited in sediments from the open Ashtamudi estuary.

Within the Kallada section of the estuary, the lowest $\delta^{13}C_{org}$ values were observed near the river inflow. These values were similar to those of river TSM from October 2002 and increased towards the south and east of the estuary. This trend indicates a

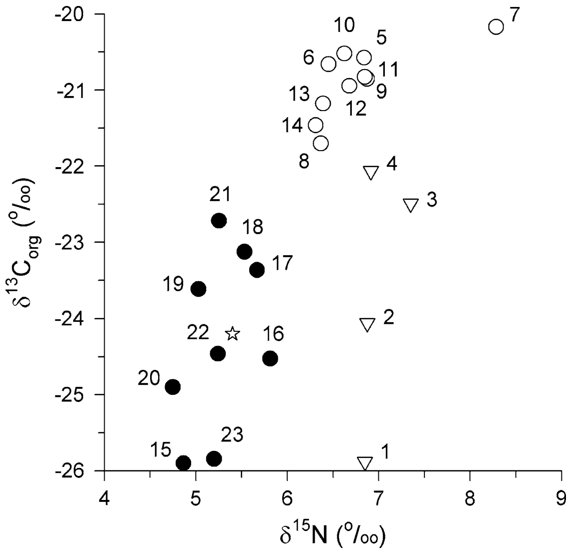

Fig. 7 Dual stable isotope composition of sediments from the Ashtamudi estuary. Sediments of the three different sections plot into distinctly different regions (*triangles* Kollam section, *open circles* open estuary, *filled circles* Kallada section), with the exception of sample A7 (see text). *Numbers* denote stations in the Ashtamudi estuary, *star* denotes the stable isotope composition of TSM from station 19 in the Kallada River in October 2002

high deposition of river-derived C in the upper estuary and an increasing portion of marine OM in the middle and lower parts of the estuary. Maximum C_{org} concentrations were observed in sediments from the Kollam section. Similar to the Kallada section, a gradient in $\delta^{13}C_{org}$ with increasing values towards the open estuary represents an increasing portion of marine OM. Outwashing from the shores and restricted tidal exchange with the open estuary and coastal sea may be responsible for a significant accumulation of terrestrial OM in the innermost part, as indicated by a $\delta^{13}C_{org}$ of −25.9‰, which is close to that of C3 plants, the predominant vegetation and soils in that area.

The observed range in $\delta^{15}N$ suggests differences in the sources and diagenetic history of the deposited N. The mean $\delta^{15}N$ of open estuary sediments of 6.8‰ is close to that of nitrate in the ocean (approx. 6‰; see Liu and Kaplan 1989) and to that of nitrate and particulate organic matter in temperate estuaries (6–9‰; Middelburg and Nieuwenhuize 2001; Middelburg and Herman 2007). From this and the dominance of saline water and marine phytoplankton during most times of the year, we infer that a major part of sedimentary N in the open estuary is of marine origin. The resuspension of sediments, which allows for intensive OM mineralization, probably caused the exceptionally high $\delta^{15}N$ of 8.3‰ and low N concentration of <0.1% at station A7. Preferential consumption of the lighter isotope may have resulted in an enrichment of ^{15}N in the remaining material. Intensive recycling has been shown to be an important process in the modification of N in turbid estuaries (Middelburg and Herman 2007). The $\delta^{15}N$ of sediments from the Kollam section was in the same range as that of sediments from the open estuary, suggesting that the N source and diagenetic transformation was similar. The mean value of 5.3‰ of sediment $\delta^{15}N$ was distinctly lower in the Kallada section than in the middle and lower reaches of the estuary. Also, it was in the range of river TSM at station 19 in October 2002, but much higher than in August 2002 (Fig. 7; Table 1). It appears that sedimentary N in the upper part of the estuary originates primarily from the river and that most of it is deposited during the rainy season. These data suggest that the upper Ashtamudi estuary is a major repository of particulate N derived from agricultural soils in the Kallada catchment.

Budgets of dissolved nutrients and suspended matter

The investigated area at the southern tip of India is located in the region of the highest sediment inputs into the ocean (Syvitski et al. 2005), and most of Kerala's rivers are small mountainous rivers according to the definition of Milliman and Syvitski (1992). These rivers usually have high sediment yields, which until recently have been underestimated in global budgets. On a global scale, the sediment yield of the Kallada River is extremely low—up to one order of magnitude lower than that of other tropical rivers and also much lower than the sediment yield of nontropical rivers (Table 5). The major reason for this may lie in the firm nature and, consequently, reduced erodibility of the predominant laterite soils and the Precambrian basement rocks of Kerala (Soman and Slukin 1987). This reduced erodibility also affects the dissolved silicate yield of the Kallada River, which is lower than that in other tropical rivers despite high runoff and high runoff temperature, both of which are favourable conditions for chemical weathering (Table 5; Gaillardet et al. 1999; Jennerjahn et al. 2006). Thus, the low supply of mineral surface area because of the reduced mechanical weathering and erosion also reduces

Table 5 Catchment size, discharge and yields of nutrients and TSM of the Kallada River and tropical and nontropical rivers of the world

River system	Area (10^3 km^2)	Discharge (km^3 year^{-1})	Nitrate-N (kg km^{-2} year^{-1})	Phosphate-P (kg km^{-2} year^{-1})	Si (kg km^{-2} year^{-1})	TSM (t km^{-2} year^{-1})
Kallada River	1.7	1.6	141	185	2,276	31
Large tropical rivers	762	473	183	28	2,514	362
Small tropical rivers	23	13	215	24	3,225	155
Nontropical rivers	729	135	325	46	1,026	68

Data on the tropical and nontropical rivers are averages taken from Global Environmental Monitoring System (2000); Jennerjahn et al. (2006)

chemical weathering and ultimately the dissolved silicate yield of the Kallada River.

Despite the intensive agriculture in Kerala, the nitrate-N yield of the Kallada River is surprisingly low; in fact, it is much lower than that in other small tropical rivers and only half as high as that in nontropical rivers (Table 5). In contrast, the phosphate-P yield of the Kallada River is extremely high when compared to levels found in other tropical and nontropical rivers. The artificial fertilizers and organic manure commonly used in Kerala have N/P ratios lower than the N/P requirements of crops and other plants (Eghball 2002; Chattopadhyay et al. 2005; Sadras 2006). This in combination with the relatively low rate of fertilizer application in Kerala suggests that N use is fairly efficient in the Kallada River catchment. Consequently, the excess P that cannot be taken up by plants is washed into the river, resulting in the extremely high phosphate-P yield when compared to other world rivers (Table 5).

Based on a statistical evaluation of data sets from 165 rivers around the globe, Smith et al. (2003) calculated that global river loads of DIN and DIP have trebled between the 1970s and the 1990s. They found that DIN and DIP yields can be sufficiently parameterized as functions of population density and runoff per area on a global scale. In the case of the Kallada River this agrees well for P, but not for N. The Kallada phosphate-P yield of 185 kg km^{-2} year^{-1} or 6 kmol $^{-2}$ year^{-1} falls into the range of 5–10 kmol DIP km^{-2} year^{-1} given for the west coast of India whereas the Kallada nitrate-N yield of 141 kg km^{-2} year^{-1} or 10 kmol km^{-2} year^{-1} is much lower than the range of 85–170 kmol DIN km^{-2} year^{-1} given (Table 5; Smith et al. 2003). In this context, it has to be mentioned that our budgets only account for phosphate-P and nitrate-N; consequently the dissolved inorganic P and N levels may be higher. With respect to the efforts of calculating global budgets, this mismatch indicates the necessity of more regional scale data and a knowledge of the river fluxes of C and nutrients and the responsible processes. It is particularly important for regions such as South and Southeast Asia which are of global relevance in terms of river fluxes and human modification of the coastal zone.

Summary and conclusions

Seasonal and downstream variations in the amount and composition of dissolved nutrients and TSM in the Kallada River results from a complex mixture of variations in natural and anthropogenic control factors. While we found little variation in the C sources, the nature of N compounds displayed distinct spatio-temporal variations along the course of the river. Nitrogen was mainly of atmospheric origin in forested area 1. Downstream differences in δ^{15}N and AA amount and composition indicate an increasing portion of OM originating from agricultural soils. The distribution patterns of biogeochemical properties of sediments indicate that most of the sediment and organic load of the Kallada River is deposited in the upper Ashtamudi estuary while the middle and lower parts are dominated by marine processes.

Despite favorable hydrological conditions for weathering and erosion, the silicate and TSM concentrations were low in the Kallada River. Reduced erosion because of the firm lateritic soils and the Pre-cambrian basement rocks might be responsible for this. Our results indicate that land use and land cover affect the biogeochemistry of the Kallada River. Elevated nutrient concentrations were observed during the rainy season some time after the major fertilizing period. On a global scale, the N yield, however, was low, most probably because of moderate N fertilizer application and efficient uptake by crop plants. In contrast, the P yield was high because of (1) high P fertilizer application owing to the P deficiency of the predominant laterite soils and (2) a fertilizer N/P ratio that is lower than the N/P requirements of crop plants. The seasonal variability in the various land uses, in the first place the tilling cycle and fertilizer application in agriculture, is an important second order control of the amount and composition of river fluxes superimposed on the natural control factors, mainly the geology, geomorphology and the hydrological cycle. However, unlike in many other regions of tropical Asia with intensive human uses and extremely high population density, the Kallada River catchment appears to be less affected by environmental degradation, as indicated by the water quality and biogeochemistry of suspended and sedimentary OM of the river and the Ashtamudi estuary. Based on the unique mixture of natural and anthropogenic factors that we found to control the fluxes and the biogeochemical composition of the Kallada River load, we infer that simple global scale parameterizations as functions of population density and runoff are not sufficient to explain the observed nutrient fluxes and yields on a regional scale. This, in turn, indicates the necessity of more regional scale data and knowledge for the calculation of robust global scale budgets of C and nutrient fluxes into the ocean.

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