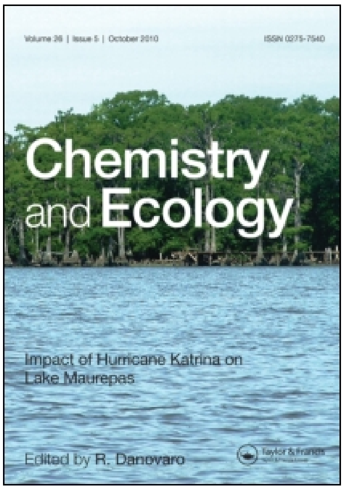

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Hydrochemistry and dissolved nutrient flux of two small catchment rivers, south-western India

K. Maya[a]; K. N. Babu[a]; D. Padmalal[a]; P. Seralathan[b]
[a] Centre for Earth Science Studies, Thiruvananthapuram, Kerala, India [b] Department of Marine Geology and Geophysics, Cochin University of Science and Technology, Kochi, Kerala, India

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Hydrochemistry and dissolved nutrient flux of two small catchment rivers, south-western India

K. MAYA*†, K. N. BABU†, D. PADMALAL† and P. SERALATHAN‡

†Centre for Earth Science Studies, Thiruvananthapuram 695031, Kerala, India
‡Department of Marine Geology and Geophysics, Cochin University of Science and Technology, Kochi 682016, Kerala, India

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This paper deals with the water chemistry and dissolved nutrient flux of two small mountainous and heavily dammed rivers—Periyar and Chalakudy—of Kerala on the south-west coast of India. The lower reaches of these rivers are affected by sea-water ingression from the Arabian Sea during the non-monsoon season. Human interference through agriculture, urbanization, and industrialization in the lower and middle stretches of the river basins induces marked concentration variations in the hydro-chemical parameters. Except for N & P, all other chemical constituents exhibit high values during the non-monsoon season. Industrial contaminants in specific locations of the Periyar river reduce the pH to lower levels. Nutrients in the two rivers reveal marked seasonal and regional concentration variations. During the monsoon season, dissolved inorganic nitrogen (DIN) predominates over dissolved organic nitrogen (DON), but the reverse trend is observed during the non-monsoon season. The Periyar river shows higher average concentrations of DIN (monsoon 801 $\mu g\,l^{-1}$ and non-monsoon 292 $\mu g\,l^{-1}$) than Chalakudy river (monsoon 478 $\mu g\,l^{-1}$ and non-monsoon 130 $\mu g\,l^{-1}$). Dissolved inorganic phosphorus (DIP) has lower average values in the monsoon season (Periyar river, 38 $\mu g\,l^{-1}$; Chalakudy river, 42 $\mu g\,l^{-1}$) than dissolved organic phosphorus (DOP) values (Periyar river, 107 $\mu g\,l^{-1}$; Chalakudy, 62 $\mu g\,l^{-1}$). The rivers show a marked difference in nutrient flux due to its difference in water discharge/basin characteristics and point/non-point sources of contaminants. The flux rates of DIN, DIP, and DOP during the monsoon are higher than during the non-monsoon season, while those of dissolved silicon (DSi), dissolved Fe (DFe), and DON are lower. On average, the Periyar river discharges 4953 $t\,y^{-1}$ of DIN and 1626 $t\,y^{-1}$ of DON to the coastal waters, and the corresponding values of the Chalakudy river are 772 $t\,y^{-1}$ and 596 $t\,y^{-1}$. The Periyar and Chalakudy rivers discharge 245 $t\,y^{-1}$ and 70.8 $t\,y^{-1}$ of DIP, respectively. The total flux of DOP is considerably higher (Periyar river 703 $t\,y^{-1}$ and Chalakudy river 101 $t\,y^{-1}$). The discharge of DSi into the Periyar river (40 193 $t\,y^{-1}$) is nearly five times higher than that in the Chalakudy river (8275 $t\,y^{-1}$). The discharges of DFe through the Periyar and Chalakudy rivers are 257 $t\,y^{-1}$ and 36.7 $t\,y^{-1}$, respectively. To sum up, this study addresses the water quality and nutrient flux of two tropical rivers and discusses the impact of urbanization and industrialization on river-water quality.

Keywords: Hydro-chemistry; Dissolved nutrient flux; Kerala rivers; South-west coast of India

*Corresponding author. Email: mayarethu@yahoo.co.in

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1. Introduction

The water chemistry of rivers in densely populated regions of the world has been undergoing tremendous modifications in the past four to five decades due to uncontrolled discharge of contaminants from point and non-point sources and other human interference [1]. Deforestation, increased agricultural activities, urbanization, industrialization, etc. in the catchment areas of rivers generate vast quantities of solid and liquid waste, which modify the river-water composition. Additionally, the uncontrolled exploitation of river bed resources for developmental activities also leads to the deterioration of fluvial systems. The enrichment or depletion of chemical constituents in a fluvial system is always in consonance with river flow characteristics and terrestrial conditions [2]. The physico-chemical and biological transformations of fluvial nutrients may have an influence on eutrophication in polluted rivers and estuaries [3].

Kerala state a densely populated region of peninsular India has 44 small rivers (catchment area $<10\,000\,km^2$), of which the basins of Periyar and Chalakudy rivers are heavily used for intense agricultural operations. The flow regimes of the rivers are also altered significantly due to damming in several places. Huge amounts of industrial and urban waste disposal are taking place in the lower reaches of the Periyar river, but such activities are considerably less in the Chalakudy river [4]. All of these, in one way or the other, lead to severe water-quality changes and shortages in the lower reaches, especially during the non-monsoon season (December – May). Therefore, an attempt is made in this paper to assess the water chemistry of the two rivers but also to evaluate the mode of transfer of nutrients through these rivers to the coastal waters.

2. Materials and methods

2.1 *Study area and environmental setting*

The Periyar and Chalakudy rivers drain through the central part of Kerala State which is in the south-western part of India (figure 1). The Periyar is the longest river of Kerala and also has the largest water potential. The characteristics of the Periyar and Chalakudy rivers are given in table 1.

Geologically, major parts of the Periyar and Chalakudy river basins are composed of crystalline rocks of Archaean age with charnockites, charnockite gneiss, hypersthene-diopside gneiss, hornblende gneiss, and hornblende-biotite and quartz-mica gneiss/biotite gneiss (composite) rock types. These crystalline rocks are intruded at many places by quartzite, pyroxene granulite, and calc granulite. Sedimentary formations ranging in age from Miocene (subsurface occurrence) to Sub-Recent overlie the crystallines along the coastal tract. The entire basin area falls under three broad physiographical units, the highland (>75 amsl), midland (75–8 amsl), and lowland (<8 amsl). Of these, the former two units cover more than 85% of the entire study area. The region receives an annual rainfall of about 3500 mm. The area enjoys a tropical humid climate, and the annual average temperature varies between 23.5 °C and 31.5 °C. Figure 2 shows the average monthly water discharge for the Periyar and Chalakudy rivers measured during the years 1985–1986 to 1994–1995.

2.2 *Sampling and analytical methods*

Surface water samples were collected in pre-washed polyethylene bottles from 19 locations (11 from the Periyar river and 8 from the Chalakudy river), during February (non-monsoon)

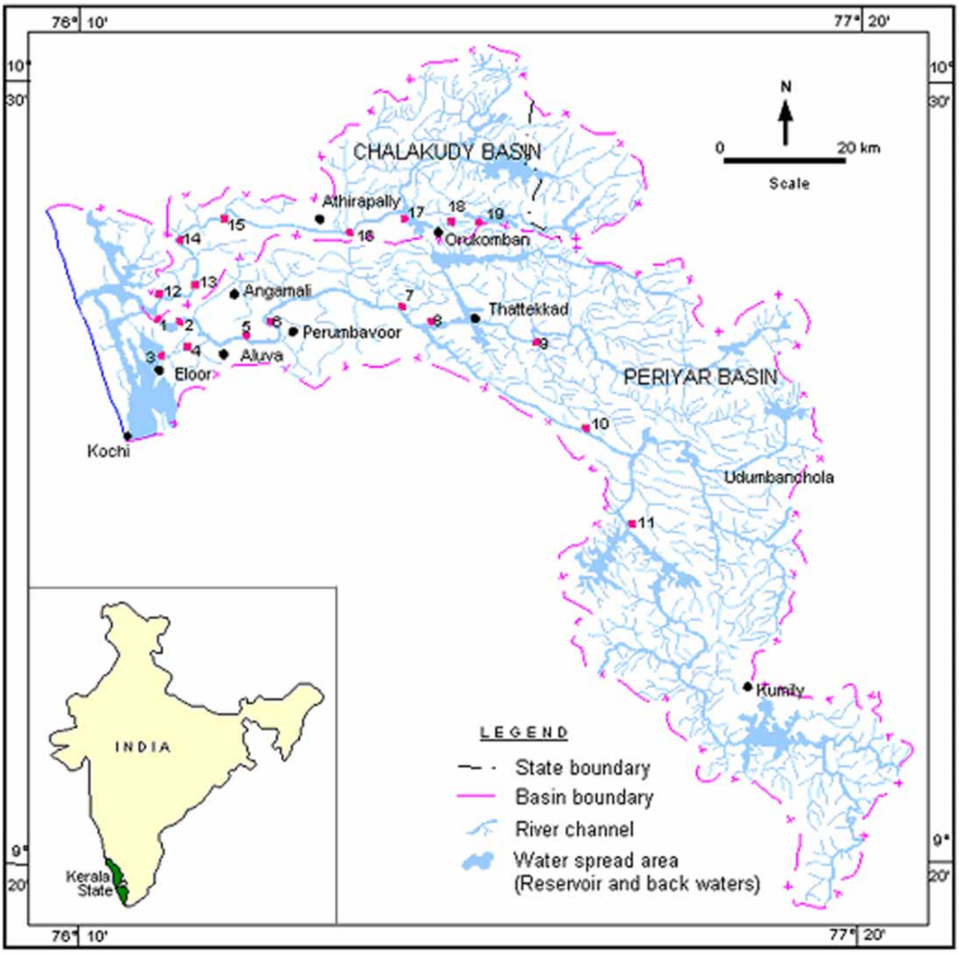

Figure 1. Study area showing sampling stations.

and July (monsoon) 2003 (figure 1). Conductivity and pH were determined at the time of sampling using a portable water-quality analyser (Multilane F/SET-3, WTW). Dissolved oxygen (DO) was fixed at the field and estimated by the Winkler method with azide modification. An unseeded dilution technique and incubation for 5 days at 20 ± 1 °C were adopted to

Table 1. Salient features of the Periyar and Chalakudy rivers.

Serial no.	River characteristics	Periyar river	Chalakudy river
1	Length (km)	244	130
2	Origin of the river (m)*	1830	1250
3	Total basin area (km^2)	5398	1748
4	Number of reservoirs	13	5
5	Number of tributaries	4	5
6	Temperature range (°C)	24–31	23–32
7	Annual Rainfall (mm)	3250	3600
8	Water discharge (Mm^3 yr^{-1})	6868	1729

Note: *Measured from mean sea level.

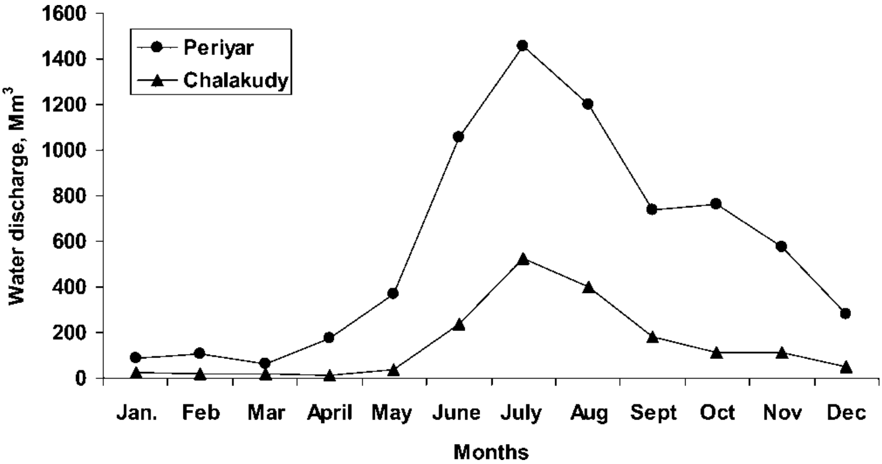

Figure 2. Average monthly discharge of water through the Periyar and Chalakudy rivers.

estimate biochemical oxygen demand (BOD). Estimations of DO, BOD, Cl, SO_4, hardness, N, P, Si, Ca, Mg, F, Fe, TDS, and TSS were carried out following standard methods [5, 6]. All nutrients and DFe were determined by colorimetry. The colour complexes of various nutrients and Fe were measured using a UV-visible spectrophotometer (Shimadzu, UV 160A).

3. Results

The water samples for the two rivers show a slightly acidic to neutral pH during both the seasons. Compared with the pH of the monsoon season, the pH of the non-monsoon season is slightly higher for the two rivers (tables 2 and 3). The Periyar river shows lower values of pH than the Chalakudy river. Figures 6–8 summarize the average values of hydrochemical parameters along with the maximum and minimum values.

The seasonal difference of pH in the Chalakudy river water is higher in the downstream stations (Nos 12–15) compared with the upstream counter parts (Nos 16–19); (figure 3). Conductivity also shows a minimal seasonal difference upstream compared with the downstream reaches where saltwater incursions are observed. The upstream zones of the two rivers have a higher DO than the industrialized/urbanized downstream stretches. Among the two rivers, the Periyar river has low DO values. The lowest DO is observed in the Eloor region of the Periyar river, influenced by effluents from chemical/fertilizer industries (tables 2 and 3). The BODs of both the Periyar and the Chalakudy river waters are higher during the non-monsoon season (Periyar: average 2.34 $mg\,l^{-1}$; Chalakudy: average 2 $mg\,l^{-1}$) than during the monsoon season (Periyar: average 1.7 $mg\,l^{-1}$; Chalakudy: average 1.5 $mg\,l^{-1}$). Also, during both the seasons, BOD values exhibit a marked increase towards downstream (figure 3). The increase is more pronounced in the lower reaches, which are contaminated by urban and industrial wastes. The concentration of HCO_3 in the Periyar (average M: 16.48 $mg\,l^{-1}$; NM: 24.5 $mg\,l^{-1}$) and Chalakudy rivers (average M: 12.5 $mg\,l^{-1}$; NM: 24.4 $mg\,l^{-1}$) reaches high values during the non-monsoon season. The low HCO_3 values tally with the corresponding low water pH. The downstream stretches of the rivers are affected by tidal incursion and show comparatively higher values of HCO_3 than the upstream reaches

Table 2. Physico-chemical parameters of Periyar river water, south-western India.

		Sampling stations										
Parameters	Period	1	2	3	4	5	6	7	8	9	10	11
pH	M	6.26	5.92	3.79	5.47	5.7	5.58	5.52	5.41	5.45	5.6	5.9
	NM	7.04	6.06	4.74	6.82	6.92	7.2	6.96	6.91	6.55	6.84	6.95
Conductivity, $\mu S\,cm^{-1}$	M	256	80.5	98.7	38.4	33.6	38.6	42	45.8	31.6	30.6	29.4
	NM	20 550	170	2890	33.2	33.4	28.8	27.6	27.8	25.6	24.8	25.9
DO, $mg\,l^{-1}$	M	5.2	5.1	4.9	6	5.9	5.8	6.3	6.7	6.3	6.6	6.5
	NM	5.3	5.4	4.3	6.7	7	7.1	7.5	7.9	7.6	7.2	7.1
BOD, $mg\,l^{-1}$	M	2.1	2.4	3.8	2.1	1.8	1.3	1	1.1	1.2	1	0.85
	NM	3.1	3.2	5.5	2.6	2.1	1.9	1.8	1.4	1.3	1.6	1.2
HCO_3, $mg\,l^{-1}$	M	15.4	17.1	6.1	20.7	18.3	15.9	18.3	20.7	18.3	15.9	14.6
	NM	85.4	24.4	7.3	17.1	19.5	17.1	20.7	19.5	19.5	20.7	18.3
Chloride, $mg\,l^{-1}$	M	85.9	22.8	29.3	8.59	7.58	7.86	7.93	8.08	7.58	7.52	7.3
	NM	9300	37.8	1403	7.32	7.32	6.12	6.72	6.88	8.54	8.54	8.48
Sulfate, $mg\,l^{-1}$	M	13.9	6.28	5.13	0.72	0.82	1.52	1.6	1.74	1.74	1.66	1.36
	NM	1070	5.71	104	0.48	0.1	0.19	0.24	0.29	0.26	0.22	0.18
Hardness, $mg\,l^{-1}$	M	37	20	19	12	11	14	14	16	10	10	10
	NM	3500	28	380	9	9	10	10	8	10	10	8
DIN, $\mu g\,l^{-1}$	M	657	864	1167	744	773	831	690	718	829	794	743
	NM	32	155	418	300	427	346	340	359	291	284	256
DON, $\mu g\,l^{-1}$	M	282	127	458	216	167	159	250	211	131	126	237
	NM	520	532	802	397	292	278	170	161	247	244	239
DIP, $\mu g\,l^{-1}$	M	40.5	39.3	48.3	33.8	38.3	40.2	42	43.5	33.8	30.8	28.4
	NM	58.1	15.8	41.1	18.5	18.5	29	16.3	13.2	13	14	13
DOP, $\mu g\,l^{-1}$	M	145	150	167	151	124	105	86	96	58	57	40
	NM	57	99	38	97	143	40	140	30	79	76	54
Fluoride, $\mu g\,l^{-1}$	M	71	76	102	46	61	68	70	63	49	48	44
	NM	1435	565	878	50	48	54	48	44	46	44	49
SiO_2-Si, $mg\,l^{-1}$	M	5.2	5.28	5.21	5.99	5.01	5.44	5.9	5.84	5.38	5.44	5.38
	NM	5.33	9.58	7.39	7.81	8.08	8.03	8.54	8.66	8.02	8.16	7.96
Ca, $mg\,l^{-1}$	M	4.81	4.41	4.41	2.81	2	2.41	3.88	4.01	2.81	2.78	2.78
	NM	160	4.41	32.1	2.4	2.4	2	1.98	2	2	1.98	2.02
Mg, $mg\,l^{-1}$	M	1.22	1.46	1.94	1.22	1.46	1.22	1.38	1.46	0.73	0.73	0.73
	NM	753	4.13	72.9	0.73	0.73	0.82	0.77	0.73	0.73	0.73	0.56
Dissolved Fe, $\mu g\,l^{-1}$	M	19.8	29.6	54.5	44.5	37.1	37.1	26	22.2	22.2	21	20
	NM	76	81	96	55	75	76	74	73	84	86	74
Total Fe, $\mu g\,l^{-1}$	M	384	890	4620	778	2900	1780	1120	1612	1167	1040	820
	NM	275	1678	955	273	1080	208	410	434	163	266	216
TDS, $mg\,l^{-1}$	M	139	48.5	58.3	25.5	17.8	26.4	27.3	30.8	25	24.8	19.1
	NM	11 630	101	1672	19.3	21.2	26.5	18.4	16.4	16.3	16	16.8
TSS, $mg\,l^{-1}$	M	6	98	20.8	40.4	13.2	89	98	129	90	78	69.5
	NM	6.9	3.5	5	2.3	15.5	1.1	2.1	1.4	1.2	2.2	2.3

Note: M: Monsoon; NM: Non-monsoon.

(figure 3). The chloride content reveals wide longitudinal variations in the two rivers. Water from the freshwater zone of the Periyar and Chalakudy rivers shows high SO_4 concentrations in the monsoon season (average Periyar $1.4\,mg\,l^{-1}$; Chalakudy: $1.8\,mg\,l^{-1}$). Fluoride shows no definite seasonal differences in the freshwater zone of the Periyar river (average

Table 3. Physico-chemical parameters of Chalakudy river water, south-western India.

		Sampling stations							
Parameters	Period	12	13	14	15	16	17	18	19
pH	M	5.42	5.39	5.54	5.65	6.34	6.44	6.49	6.80
	NM	7.18	7.47	7.22	7.12	7.20	7.23	7.28	7.32
Conductivity, $\mu S/cm^{-1}$	M	44.6	36.4	31.5	35.8	26.5	25.9	25.4	24.9
	NM	17 090	210	61.0	55.0	39.0	36.0	35.2	34.8
DO, $mg\,l^{-1}$	M	5.5	5.4	5.2	6.4	7.1	7.2	6.9	6.8
	NM	6.0	6.1	6.4	6.7	7.2	7.4	7.0	7.1
BOD, $mg\,l^{-1}$	M	2.2	2.4	2.1	1.4	1.2	0.9	1.0	0.95
	NM	2.9	3.0	2.8	1.9	1.7	1.2	1.5	1.2
HCO_3, $mg\,l^{-1}$	M	13.4	13.4	13.4	14.6	11	9.8	12.2	12.2
	NM	80.5	14.6	15.9	19.5	17.1	15.9	14.6	17.1
Chloride, $mg\,l^{-1}$	M	12.6	10.6	7.58	9.60	8.59	8.12	8.26	7.38
	NM	8235	50	14.0	13.0	12.0	11.5	11.7	10.9
Sulfate, $mg\,l^{-1}$	M	1.54	2.36	2.56	2.36	2.05	1.13	1.28	0.82
	NM	1040	1.65	1.08	0.44	BDL	BDL	BDL	BDL
Hardness, $mg\,l^{-1}$	M	14	12	8.0	9.0	8.0	7.8	8.2	8.0
	NM	2950	70.0	13.0	11.0	10.0	10.2	9.5	9.5
DIN, $\mu g\,l^{-1}$	M	438	497	585	631	465	440	426	342
	NM	308	217	167	125	58	56	60	52
DON, $\mu g\,l^{-1}$	M	536	420	406	308	299	306	298	350
	NM	318	220	150	111	89	98	76	64
DIP, $\mu g\,l^{-1}$	M	47.3	45.0	47.3	58.5	38.3	36.5	32.0	28.0
	NM	79	40	29	26	19	20	17	18
DOP, $\mu g\,l^{-1}$	M	88	53	92	38	54	52	62	60
	NM	36	32	27	23	20	15	25	21
Fluoride, $\mu g\,l^{-1}$	MN	92	81	49	73	11	12	10	9.8
	NM	1363	110	90	85	27	29	26	25
$SiO_2{-}Si$, $mg\,l^{-1}$	M	3.92	4.54	5.13	4.55	4.50	4.40	4.10	3.97
	NM	7.77	9.31	9.35	9.12	8.98	8.72	9.04	8.72
Ca, $mg\,l^{-1}$	M	2.40	3.21	2.40	1.60	1.20	1.10	1.00	1.02
	NM	160	22.4	2.20	2.01	1.80	1.60	1.70	1.62
Mg, $mg\,l^{-1}$	M	1.94	0.97	0.49	0.49	0.49	0.49	0.49	0.52
	NM	619	3.4	0.97	0.67	0.67	0.58	0.67	0.63
Dissolved Fe, $\mu g\,l^{-1}$	M	24.7	17.3	21.7	18.8	12.1	14.2	11.9	12.0
	NM	73	82	87	73	59	56	60	58
Total Fe, $\mu g\,l^{-1}$	M	529	973	589	629	745	820	790	810
	NM	301	429	324	210	172	160	156	160
TDS, $mg\,l^{-1}$	M	30.6	25.6	21.4	24.2	20.3	18.2	18.9	16.1
	NM	10 200	132	37.0	28.0	24.0	23.0	22.8	22.8
TSS, $mg\,l^{-1}$	M	11.6	16.0	18.0	35.8	66.4	74.5	62.4	57.6
	NMN	11.2	9.2	4.0	2.0	2.6	2.9	2.3	2.3

Note: M: Monsoon; NM: Non-monsoon; BDL: Below the detection limit.

M: 56.1 $\mu g\,l^{-1}$; NM: 47.9 $\mu g\,l^{-1}$), while marked variations are observed in the Chalakudy (average M: 42.2 $\mu g\,l^{-1}$; NM: 47.0 $\mu g\,l^{-1}$) river. During the non-monsoon period, both the Periyar and Chalakudy rivers show similar fluoride contents in freshwater zone, while during the monsoon season, the average fluoride content in the Periyar river shows higher values than that of the Chalakudy river (figure 4).

Nitrogen is estimated in this study as dissolved inorganic nitrogen (DIN) and dissolved organic nitrogen (DON). Of the three species of DIN ($NO_2{-}N$, $NO_3{-}N$, and $NH_3{-}N$), $NO_3{-}N$ values are markedly higher than the other two species, $NO_2{-}N$ and $NH_3{-}N$. $NO_2{-}N$ and $NH_3{-}N$ are recorded only at marginal levels in almost all stations except the regions influenced by urban/industrial waste-water discharges. In these rivers, the DIN exhibits markedly high seasonal and regional variations (figure 4). In general, DIN values are two

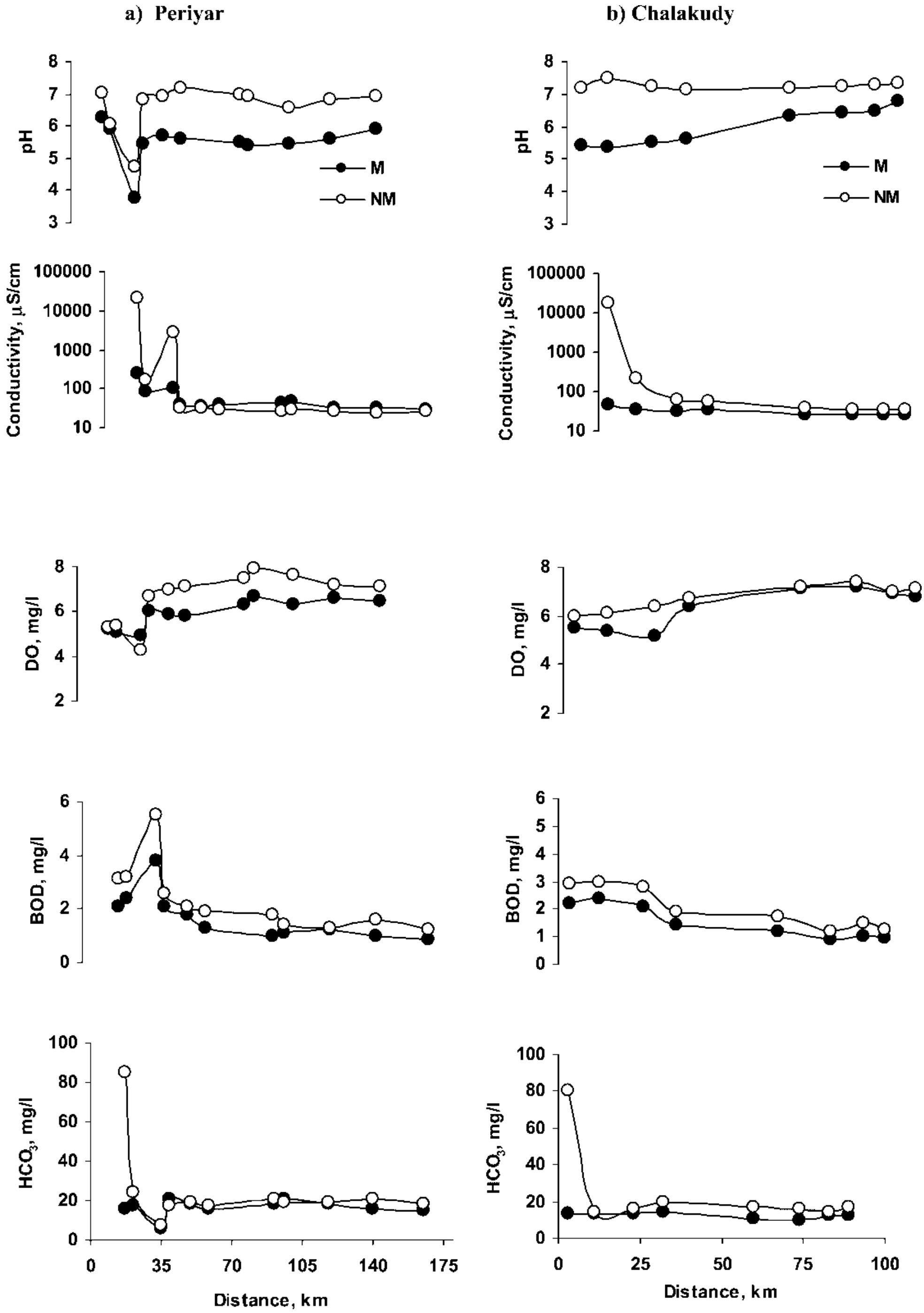

Figure 3. Downstream variations of pH, conductivity, DO, BOD, and HCO_3 in the Periyar and Chalakudy rivers.

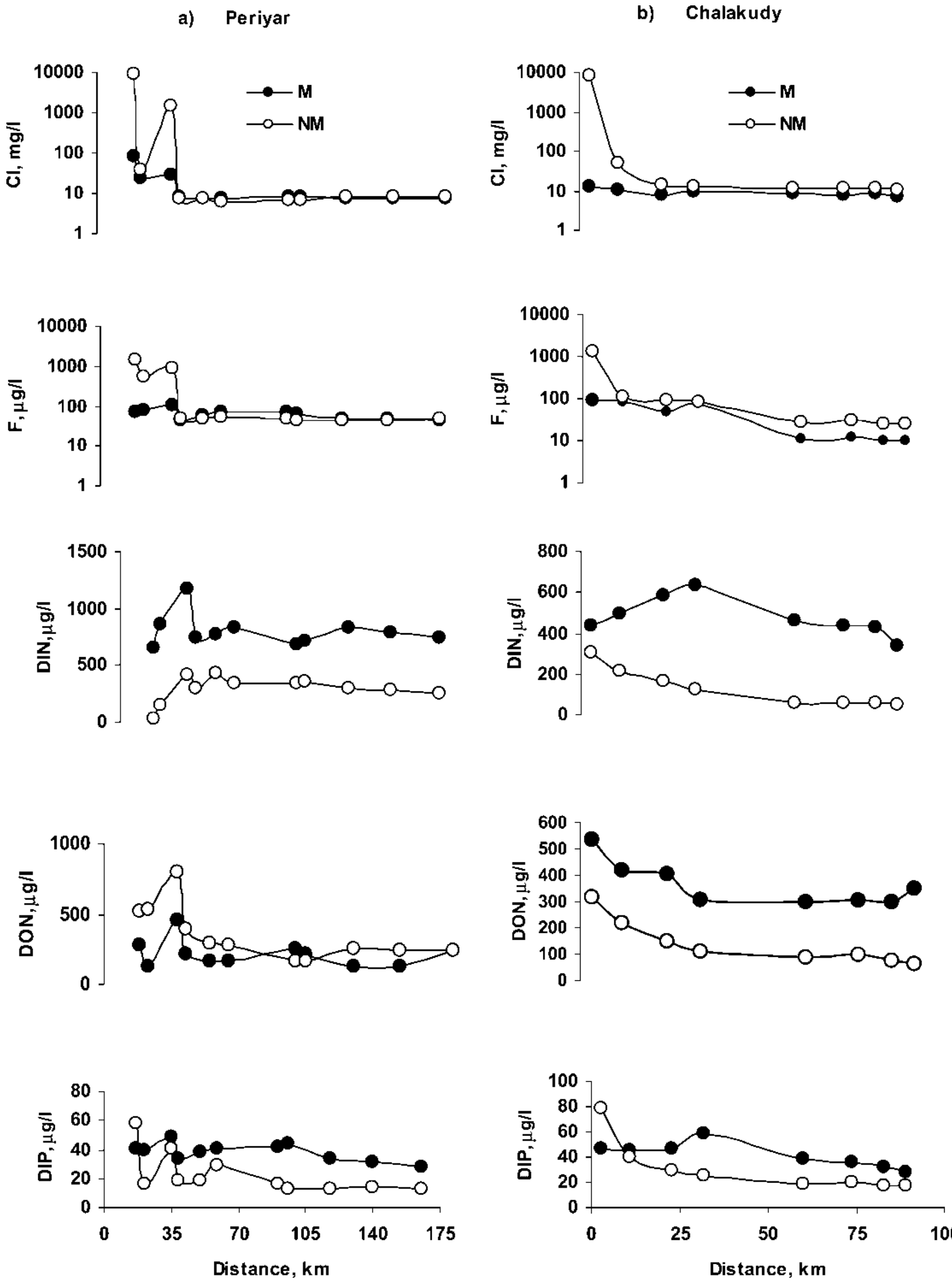

Figure 4. Downstream variations of Cl, F, DIN, DON, and DIP in the Periyar and Chalakudy rivers.

to three times higher during the monsoon compared with non-monsoon values (table 4). The DON records a comparatively lower range of concentrations in the monsoon season, but in the non-monsoon season, its content is much higher with respect to DIN. The trend is more pronounced in the Periyar river compared with Chalakudy river. Like nitrogen the dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP) species are also

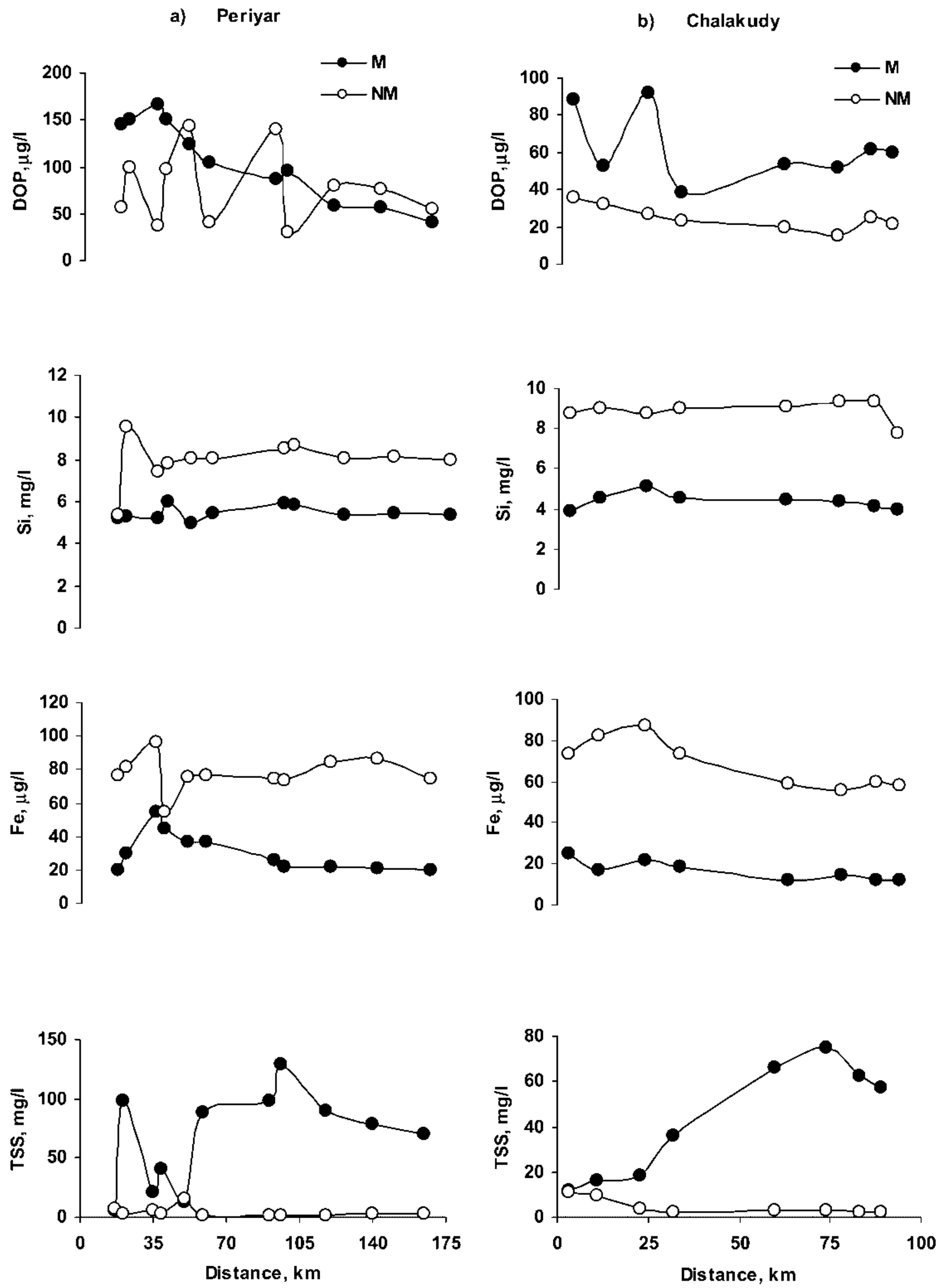

Figure 5. Downstream variations of DOP, Si, Fe, and TSS in the Periyar and Chalakudy rivers.

estimated. Phosphorus forms are detected only in lower concentrations in both the Periyar and Chalakudy rivers. At the same time, their regional and seasonal behaviour are generally in consonance with the nitrogen forms. An inter-comparison of the two forms of phosphorus, DIP and DOP, between the Periyar and Chalakudy rivers reveals that the Periyar river

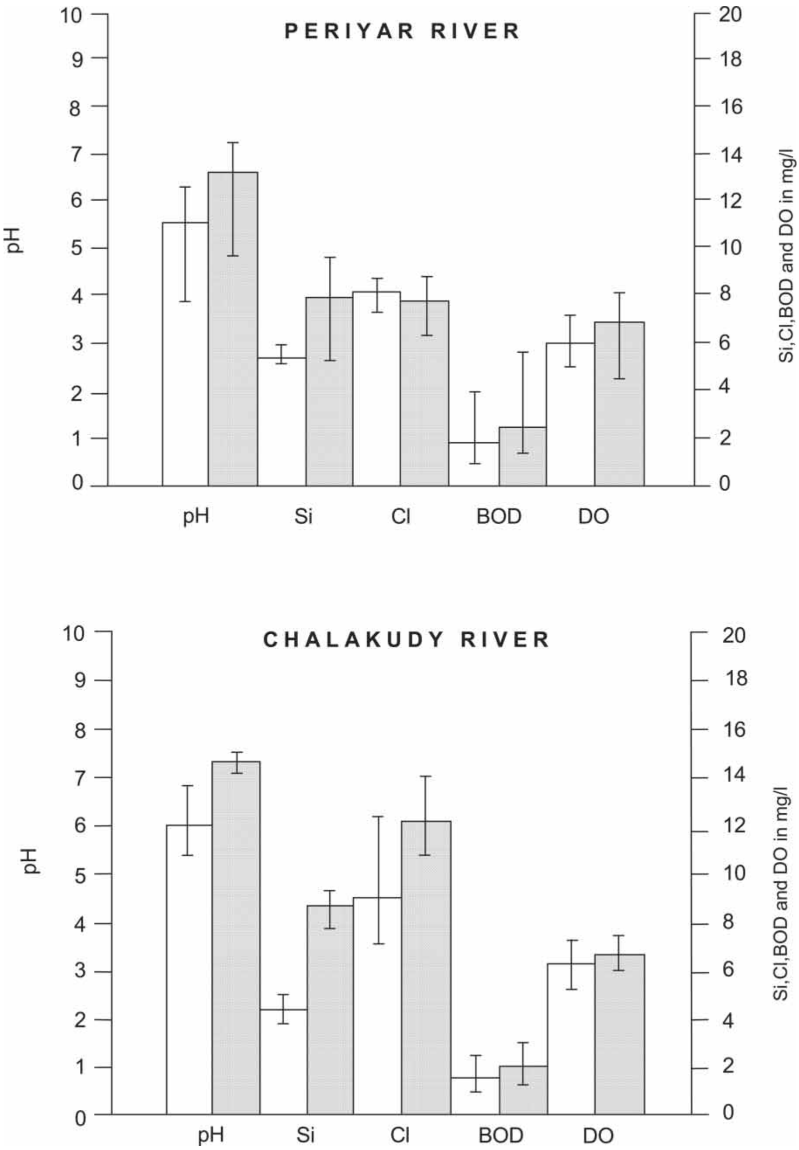

Figure 6. Histogram showing the average concentration of pH, Si, Cl, BOD, and DO in the Periyar and Chalakudy rivers. Vertical bars in each block represent the respective ranges of each parameter.

is enriched with DOP (average M: 107 $\mu g\,l^{-1}$; NM: 77 $\mu g\,l^{-1}$) more than DIP (average M: 38 $\mu g\,l^{-1}$; NM: 23 $\mu g\,l^{-1}$) during both seasons. In the case of Chalakudy river, during the monsoon season the average DOP (62 $\mu g\,l^{-1}$) shows a higher concentration than the corresponding DIP (42 $\mu g\,l^{-1}$) but in the non-monsoon period, DIP (31 $\mu g\,l^{-1}$) is higher than DOP (24 $\mu g\,l^{-1}$). During the monsoon season, the Periyar river shows a slightly higher average concentration of silicon (average 5.46 $mg\,l^{-1}$) than the Chalakudy river (average 4.38 $mg\,l^{-1}$), while a reverse trend is observed during the non-monsoon (Periyar: 7.96 $mg\,l^{-1}$; Chalakudy: 8.88 $mg\,l^{-1}$). The freshwater zones of the Periyar and Chalakudy rivers reveal marked regional and seasonal differences in total dissolved solid (TDS) contents (tables 2 and 3). The total suspended solid (TSS) contents of the two river waters are several-fold higher during the

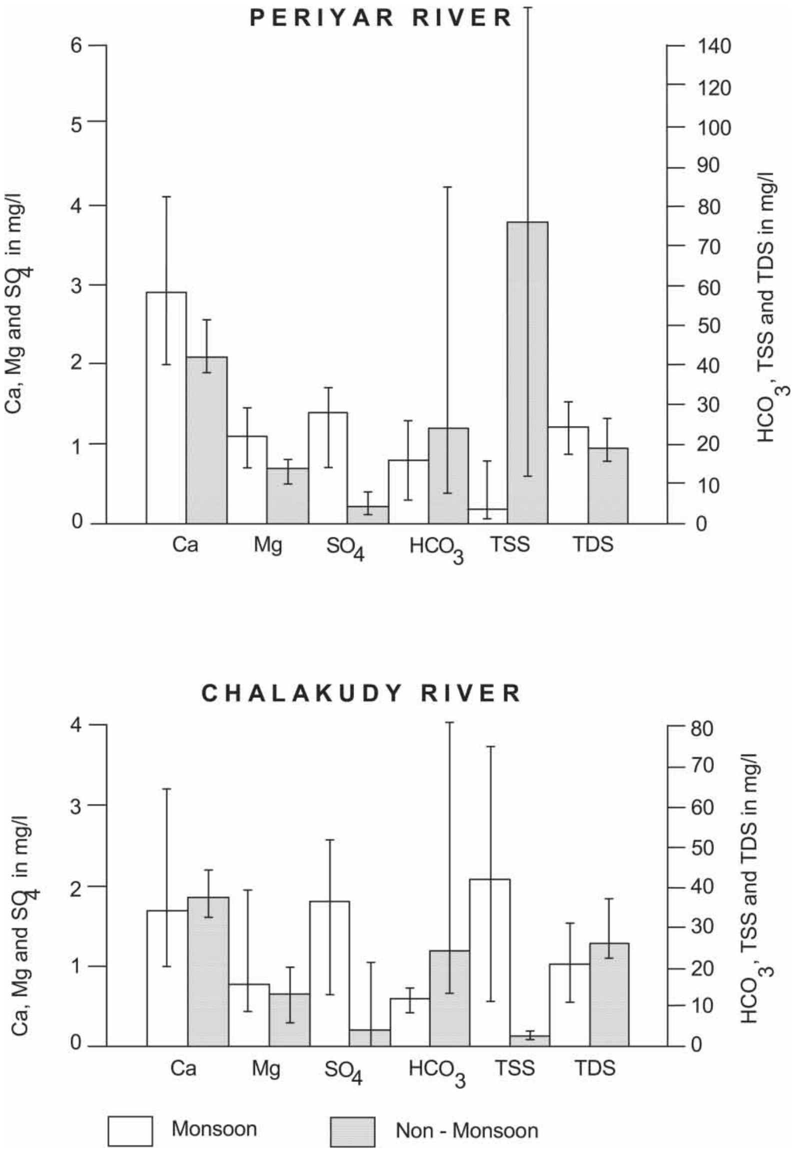

Figure 7. Histogram showing the average concentration of Ca, Mg, SO_4, HCO_3, TSS, and TDS in the Periyar and Chalakudy rivers. Vertical bars in each block represent the respective ranges of each parameter.

monsoon (average Periyar: 66.5 mg l^{-1}; Chalakudy: 42.8 mg l^{-1}) season compared with the corresponding non-monsoon (average Periyar: 3.95 mg l^{-1}; Chalakudy: 4.6 mg l^{-1}) values. The Ca in the freshwater zone of the Periyar and Chalakudy rivers shows marked regional and seasonal variations. The concentration of Mg in the freshwater region of the two rivers indicates more seasonal difference in the Periyar river than in the Chalakudy river. The two river waters reveal a wide seasonal variation of DFe (figure 5). Non-monsoon values of both rivers are three to four times higher than the corresponding monsoon values. Contrary to dissolved Fe, the total Fe exhibits a higher concentration in the monsoon season than in the non-monsoon season, due to the presence of a high load of suspended particulates in the monsoon water.

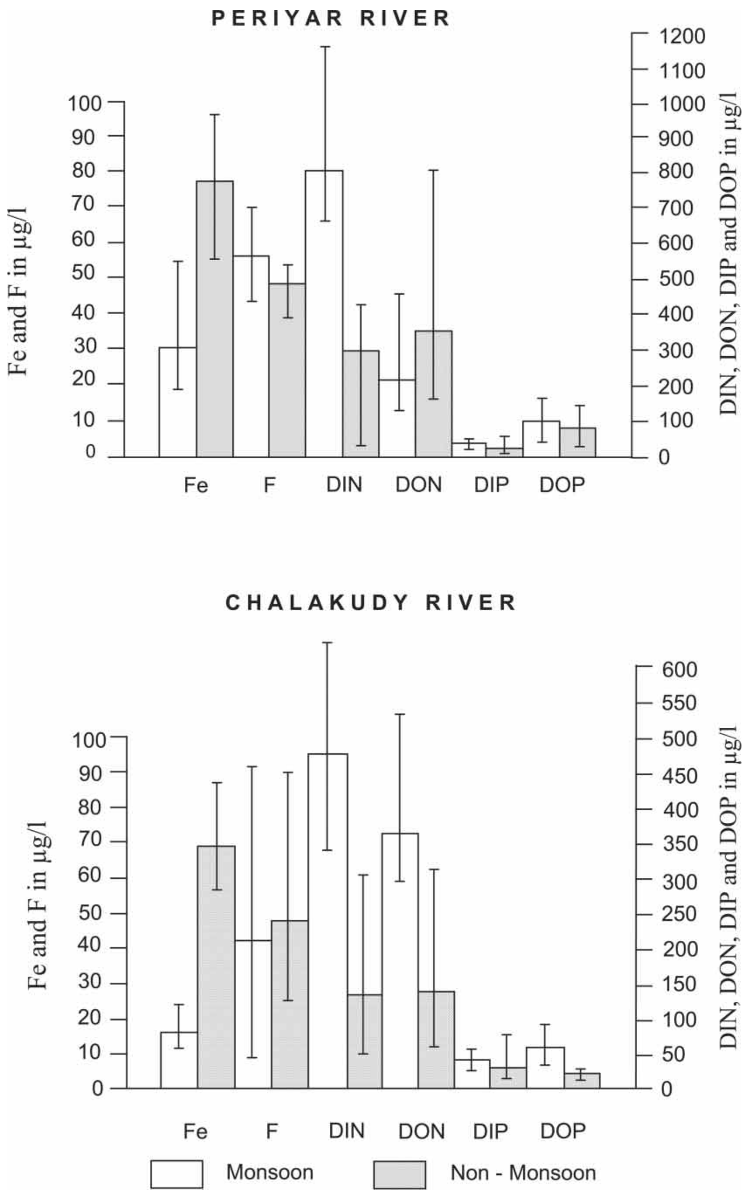

Figure 8. Histogram showing the average concentrations of Fe, F, DIN, DON, DIP, and DOP in the Periyar and Chalakudy rivers. The vertical bars in the block represent the respective ranges of each parameter.

4. Discussion

4.1 *Water-quality changes*

Regional and seasonal variations of water quality in the Periyar and Chalakudy rivers are controlled by anthropogenic effects and hydrological cycles. pH, DO, BOD, HCO_3, and Fe concentrations are higher during the non-monsoon period, whereas nutrients show enrichment during the monsoon period. The upstream stretches of the two rivers are under dense

Table 4. Dissolved nutrient flux rate for the Periyar and Chalakudy rivers, south-western India.

Particulars		Periyar river		Chalakudy river	
		M	NM	M	NM
Water discharge (Mm^3)		5790	1078	1573	156
DIN	Flux rate, $\mu g\,l^{-1}$	801	292	478	130
	Seasonal discharge, Tons	4638	315	752	20.3
DON	Flux rate, $\mu g\,l^{-1}$	215	353	365	141
	Seasonal discharge, t	1245	381	574	22
DIP	Flux rate, $\mu g\,l^{-1}$	38	23	42	31
	Seasonal discharge, Tons	220	25	66	4.8
DOP	Flux rate, $\mu g\,l^{-1}$	107	77	62	24
	Seasonal discharge, Tons	620	83	97.5	3.7
DSi	Flux rate, $mg\,l^{-1}$	5.46	7.96	4.38	8.88
	Seasonal discharge, Tons	31 613	8580	6890	1385
DFe	Flux rate, $\mu g\,l^{-1}$	30	77	16.6	68
	Seasonal discharge, t	174	83	26.1	10.6

forest cover, whereas the midlands and lowlands are occupied by agricultural lands and settlements, and hence anthropogenic impact is more pronounced at the lower reaches of the rivers. Furthermore, during the non-monsoon season, the lower stretches of Periyar and Chalakudy rivers up to 35 km and 11 km inland, respectively, are affected by sea-water ingression.

High flow in the monsoon season induces marked changes in water quality in the two rivers. The pH and DO decrease markedly in the monsoon season, due to the influence of acidic rain water and the presence of oxygen-demanding organic substances. Since parts of the uplands and midlands of the river basins are mainly used for agricultural purposes, the heavy monsoon flows carry residual nutrients from the soil into the rivers and hence lead to high values during the season. Nutrient-enriched water in the monsoon season consumes a large quantity of DO to oxidize it into stable end products, thus lowering the DO [7]. When the organic load overweighs the assimilative capacity of the river system also lowers DO below its threshold concentration ($5\,mg\,l^{-1}$). The industrially prone Eloor region (station 3) of the Periyar river shows low DO values due to the introduction of vast quantities of industrial effluent (table 2). During the non-monsoon season, ammonia constitutes the major component (average $351\,\mu g\,l^{-1}$) of DIN in this locality, whereas in all other locations, ammonia is absent in the same period. A reduction of adequate freshwater flow through the river channel during the non-monsoon season, owing to heavy damming, and accumulation of contaminants are the possible reasons for this high ammonia content. Compared with Periyar water, DO is more enriched in Chalakudy, where industrial contamination is much lower. Monsoon water dilutes the river contamination and lowers the high BOD prevailing in the non-monsoon period. All nutrient species of nitrogen and phosphorus show a two to threefold increase during the monsoon compared with the non-monsoon season. However, the silicon concentration is drastically reduced in the monsoon season because of the dilution effects [8]. The flux rate of silicon through fluvial systems is generally high during the non-monsoon period due to weathering, the intensity of which is positively correlated with temperature and pH conditions that prevailed in the season [9, 10]. The TSS of the two rivers is moderately higher during the monsoon season and also correlates with the lower amount of dissolved phosphorus for the same period. The particulate forms are the main carriers of phosphorus compared with the dissolved forms in the river systems of this region; at the same time, nitrogen species are mainly discharged in the dissolved state [11].

During the monsoon season, the two river waters exhibit high concentrations of DIN (average Periyar, $801\,\mu g\,l^{-1}$; Chalakudy, $478\,\mu g\,l^{-1}$) than DON (average Periyar, $215\,\mu g\,l^{-1}$; Chalakudy, $365\,\mu g\,l^{-1}$). The corresponding average DIN and DON in the non-monsoon season are $292\,\mu g\,l^{-1}$ and $353\,\mu g\,l^{-1}$ for the Periyar river, and $130\,\mu g\,l^{-1}$ and $141\,\mu g\,l^{-1}$ for the

Chalakudy river. The major sources of inorganic nitrogen are agricultural residues through land runoff and from industrial effluents, while organic nitrogen mainly originates from sub-urban/domestic effluents and from the overflow of monsoon water through contaminated lands. The highly different values of DIN and DON in Periyar river compared with those of the Chalakudy river can be attributed to substantial contributions from industrial effluents in the former river. During the non-monsoon period, the concentration of DON in both rivers is higher than DIN, because of the reduced water discharge. Furthermore, the difference between DIN and DON in the non-monsoon season and its increase downstream can be linked to an enhanced flux of urban contaminants along the same stretch. Contaminants of urban origin contribute more bio-available DON than those of agricultural/forest origin [12]. The high contribution of DON may play a vital role in coastal food webs and nitrogen cycles [13]. The large differences in DON and DIN in Periyar with respect to the Chalakudy river water could be explained in light of enhanced urbanization in the former river basin.

4.2 *Dissolved flux estimations*

More than 80% of water discharge through the Periyar and Chalakudy rivers occurs during the monsoon period. On average, the Periyar river discharges about 5790 Mm^3 of water during the monsoon and 1078 Mm^3 of water during the non-monsoon seasons. The corresponding values for the Chalakudy river are 1573 Mm^3 for the monsoon and 156 Mm^3 for the non-monsoon season. From the flux rate of nutrients and water-discharge quantities, the total seasonal discharge of nutrients discharged through the two rivers is computed and tabulated (table 4). The total fluxes of all nutrient species through both rivers are markedly higher in the monsoon season than in the non-monsoon season. The total flux of DIN during the non-monsoon season is meager compared with that of the monsoon period. The discharge of DIN during the non-monsoon period is 6.36% of annual discharge in the Periyar river, while it is only 2.63% in the Chalakudy river. The discharge of DON in the Periyar river during the monsoon period (76.6% of the annual quantity) is significantly lower than in the Chalakudy river (96.3% of annual quantity). DIP and DOP also exhibit wide seasonal differences in flux pattern. The monsoon and non-monsoon contributions of DIP in the Periyar river are 89.8% and 10.2%, respectively, while the corresponding values in the Chalakudy river are 93.2% (monsoon) and 6.8% (non-monsoon). During the non-monsoon season, a higher quantity of DOP is discharged through the Periyar river (11.8%) than through the Chalakudy river (3.7%). Similarly, high percentages of Si and Fe discharges are observed in the Periyar river during the non-monsoon period compared with the Chalakudy river. The non-monsoon values for Si in the Periyar and Chalakudy rivers are 21.3% and 16.7%, respectively, while the corresponding values for Fe in the same period are 32.3% (Periyar river) and 28.9% (Chalakudy river). The ratio of annual water discharge quantities (water $\text{discharge}_{\text{Periyar}}$/water $\text{discharge}_{\text{Chalakudy}}$) of the rivers Periyar and Chalakudy is about 4, while the corresponding ratio of their 'basin areas' is 3. The nutrient flux values for the two rivers exhibit even higher ratios, indicating a greater nutrient flux through the Periyar river than the Chalakudy river. Thus, the flux ratio of DIN in the Periyar and Chalakudy rivers ($\text{DIN}_{\text{Periyar}}/\text{DIN}_{\text{Chalakudy}}$) is 6.41, while that of DOP and dissolved Fe are 6.96 and 6.95, respectively. Only DON reveals a lower ratio than the water-discharge ratio or basin-area ratio.

5. Conclusion

The water quality of the Periyar and Chalakudy rivers has been assessed, and the major contributors of DIN and DIP have been found to be from agricultural sources, while DON and

DOP originate from urban agglomerations. Concentrations of N and P increase downstream while Si concentrations decrease in the same direction in both seasons. The main factor responsible for dissolved silica in rivers is the weathering process. The overall water chemistry of the two rivers is controlled by weathering as well as precipitation. Damming plays a vital role in reducing the flux of nutrients, especially Si. Sea-water intrusion in the lower stretches of the two rivers is the result of a low flow regime, especially in the summer due to the construction of many dams in the upper river catchments. Of the two rivers, the Periyar river has a higher amount of contamination owing to a higher degree of urbanization, industrialization, and agricultural activities in the river basin. The two rivers receive contaminants from many sources and through several outlets, and hence the water quality shows a wide longitudinal variation.

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