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Full Length Research Paper

Natural and anthropogenic determinants of water quality changes in a small tropical river basin, SW India

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Water quality of surface and subsurface sources of densely populated regions of the world has been undergoing marked changes over the past few decades consequent to rapid economic development and /or urbanisation. Lack of adequate base-line data on the status of water quality is a major setback challenging wise use and management of these life sustaining systems. The situation is rather alarming in the small rivers of many tropical countries as these systems are more responsive to economic developments. In the present investigation, an attempt has been made to examine the chemical quality of the various water sources in a small river basin in the south western coast of India- the Neyyar River Basin (NRB) in Kerala State- as an example. The region including the basin area of Neyyar is undergoing fast economic development since early 1970's. A total of 17 chemical parameters (pH, EC, DO, alkalinity, chloride, sulphate, Ca, Mg, Na, K, total hardness, NO_2-N, NO_3-N, P-inorg, SiO_2, TSS and TDS) has been studied in the different water sources such as river (Reservoir, Mainstream and Estuary), irrigation canals (Left and Right Bank Canals), wells and springs of the NRB during summer season, which is the drinking water deficit period in the region. The study reveals that except pH and DO of a few samples, all the other water quality parameters are well within the water quality standards set by various national and international agencies. A comparative evaluation of the hydrochemical parameters of NRB with that of the other important minor and major rivers shows that except chloride, all the other parameters are recorded in lower concentrations in NRB as well as the other small mountainous rivers in the south-western coast of India.

Key words: Surface and subsurface water sources, water quality, small catchment rivers, South-western coast of India.

INTRODUCTION

Freshwater resources need special care and attention to make it available sustainably for the present and future generations. Water is vital for agriculture, industries and almost all the other human activities. Ensuring uninterrupted fresh water supply is a greatest challenge the water managers of the world have to face in the coming decades (Bonnel, 1993; Clarke, 1993; Biswas, 1993; Rosegrant, 1995; Longe and Enekwechi, 2007). Being limited in quantity, fresh water resources -both surface and subsurface - need to be wisely conserved and cautiously managed for the benefit of the present and future generations. With varying degrees of success, mankind have corrected, to some extent, the imbalance by storing water in reservoirs and also channelling the stored water to the needy areas. However, water pollution from industry, agriculture and urban centres still makes the situation complex (Yang and Jiang, 2007) as the quality and quantity of fresh water resources are critically affected by these activities (Ahearn et al., 2005; Jarvie et al., 2006; Li et al., 2008; Padmalal et al., 2011). Reports reveal that inferior quality water is often used to meet the fresh water demand in many parts of the world (Olayinka, 2004; Phiri et al., 2005). The quality of surface and subsurface water is a function of natural influences and human activities. In the absence of human influences, water quality would be determined solely by natural processes like weathering of crustal rocks, atmospheric fall outs, leaching of organic matter and nutrients from soil, hydrological factors that lead to runoff, and biological processes in the living world

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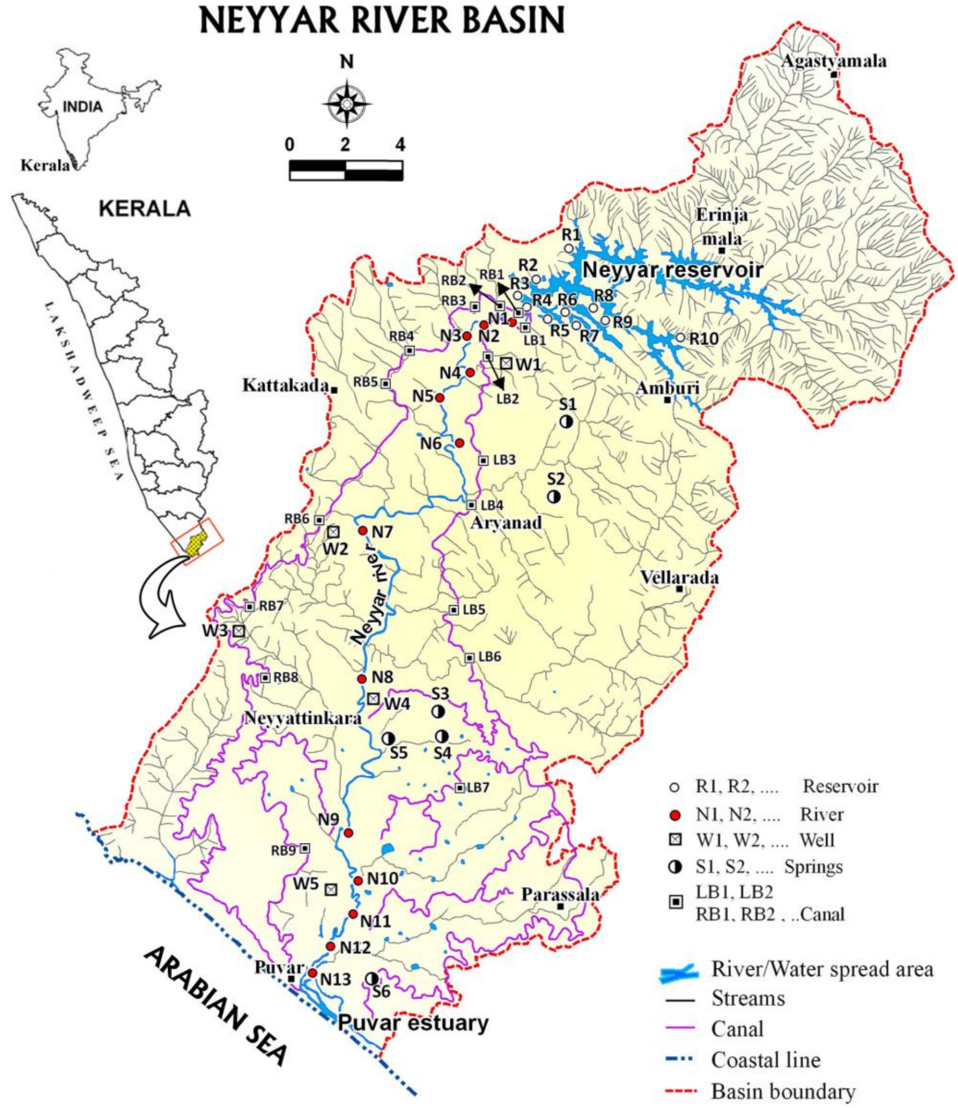

Figure 1. Study area showing drainage characteristics and sampling stations.

(Stark et al., 2000;UNEP, 2006). It is now widely accepted that water management practices must be integrated on river basin mode for achieving beneficial results. Each water source should be monitored with utmost care and precision for laying down strategies for the effective conservation and management of the pristine water resources. The water related issues are very critical in the small catchment rivers of developing economies with high incidence of human stress (Padmalal et al., 2011). But the lack of adequate data on the water quality of the different water sources of small catchment river basins is a major lacuna challenging wise utilization and management of the water resources in such basins that are more responsive to human interventions. Therefore, an attempt has been made in the present paper to address the water quality of the different water sources in one of the important small catchment rivers in the south-western coast of India, the Neyyar river basin, where the demand of water is rising exponentially over the years in tune with increase in population and economic development.

NEYYAR RIVER BASIN AND GEO-ENVIRONMENTAL SETTING

The Neyyar is a 6th order river originating from Agasthya *malai* in the Western Ghat mountain ranges at an elevation of about 1866 km above sea level. This small catchment mountainous river flows through highly varied geologic and physiographic provinces of the area and empties into the Arabian Sea near Puvar (Figure 1). The river basin lies between 8° 15´ to 8° 40´ north latitudes and 77 to 77° 20´ east longitudes. Kallar and Karavalliyar

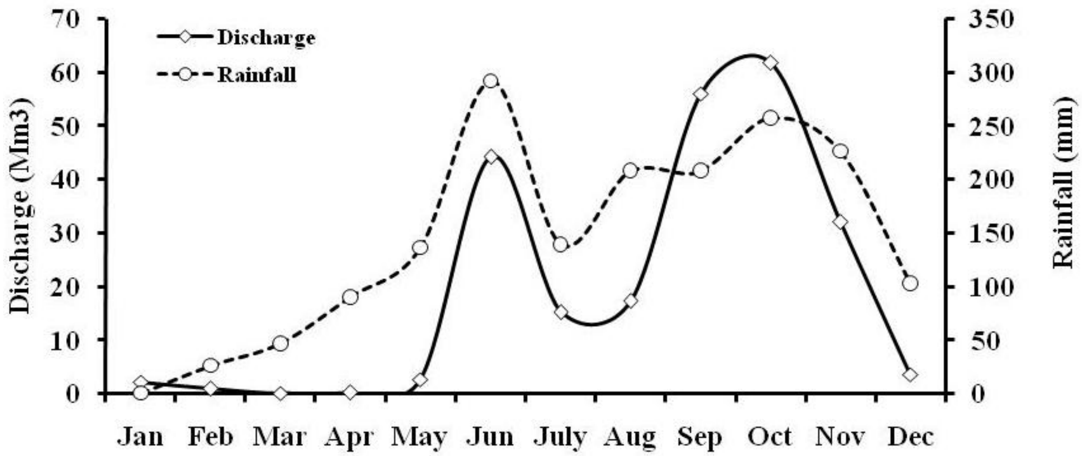

Figure 2. Monthly variations of river water discharge and rainfall in the Amaravila guaging station of Neyyar river basin.

are the major tributaries of the river. The river is perennial and discharges 433 x 10^6 m^3 of water into the Arabian Sea (CWRDM, 1995). The monthly variations of water discharge through the river and the rainfall received in the basin are depicted in Figure 2. The river discharge during premonsoon, monsoon and postmonsoon seasons are 5.6, 132.6 and 97.3 Mm^3, respectively (source: Irrigation Department, Government of Kerala). The atmospheric temperature in the basin varies between 24 and 32°C. The river basin receives an average rainfall of 2380 mm; a major portion (60%) is contributed by monsoon showers. The area enjoys a tropical humid climate. Water quality problems are found to be severe in premonsoon period (January to May; summer season in Kerala) every year. Geologically the basin is composed of Archaean crystallines and, Neogene and Quaternary sediments. The Neyyar River Basin (NRB) exhibits diverse landuse. A greater portion of the basin is occupied by agricultural land including plantation crops (68.45%) followed by natural vegetation/forest cover (24.16%). The Barren rocky/stony wasteland is seen mainly in the forest area (3%). Settlement/built-up area and water spread area comprises 2.1 and 2.18% respectively (Sheeja et al., 2010). A reservoir has constructed in the upland of NRB in 1952 near Kallikkadu for augmenting agricultural productivity. The irrigation project, hereafter referred to as the Neyyar Irrigation Project (NIP), is meant for irrigating an area of 15528 *ha* of agricultural land spreading in the Nedumangadu and Neyyattinkara taluks in Thiruvananthapuram) district of Kerala State (Figure 6) and Kuzhithurai taluk in Kanyakumari district of Tamil Nadu State. The NIP has two major canals: 1- the Right Bank Canal (RBC) and 2- the Left Bank Canal (LBC). The RBC takes off from the dam at a bed level of 180 feet and has a length of 33 km with a capacity of 110 cusecs. The area benefited by the RBC alone is 1494 *ha* in the NRB. The Left Bank Canal (LBC) was originally designed for a water discharge of 270 cusecs. The length of the canal is 38 km and is directly feeding 133 *ha* of land in the NRB.

METHODOLOGY

A systematic field work was carried out for the collection of primary and secondary data on various aspects of the different water sources of the NRB. A total of 50 water samples, [10 from reservoir, 11 from river, 2 from estuary, 16 from irrigation system (9 - RBC and 7 – LBC), 5 from dug wells and 6 from natural springs] were collected (Figure 1) during March 2011. The pH and EC were determined at the time of sampling using a portable water quality analyser (Multilane F/SET -3, WTW). The dissolved oxygen (DO) content in the samples was estimated by Winkler method with azide modification. Chloride, total alkalinity, total hardness (TH), calcium (Ca) and magnesium (Mg) were determined by titration method (Trivedi and Goel, 1986). Sulphate content in the sample was determined by turbidimetry. The sodium (Na) and potassium (K) contents in the samples were determined using flame photometer. Standard methods (APHA, 1985) were followed for the determination of all the other parameters in the water samples of the study area. Dissolved nutrients were estimated colorimetrically by UV- visible spectrophotometer (Model: Shimadzu UV 160A) after filtration of water through 0.45 um Millipore membrane filters (APHA, 1985). The dissolved inorganic carbon (DIC) is measured by using total organic carbon analyser (Model: A-TOC-HT).

RESULTS

pH and DO

Water samples collected from the different water sources of NRB are slightly acidic, with a pH range of 4.84 to 6.8 (Table 1). On an average, the river (6.31), reservoir (6.50), estuary (6.26) and the canal (LBC, 6.63; RBC, 6.21) environments showed almost similar pH values. Contrary to the surface water, the spring water samples are more acidic (av. 5.26) than that of the well waters (av. 5.9). The pH of most of the samples collected in different sub-environments of NRB falls below the prescribed limit of WHO, BIS and ICMR (Table 1). The average DO in NRB varies between 4.01 (Well water) and 8.9 mg L^{-1} (LBC). The average DO content in the river, reservoir, estuary and springs are 7.48, 8.06, 6.3 and 4.56 mg L^{-1} respectively. Among the various water samples collected from NRB, the spring water registered the lowest (1.85 mg L^{-1}) and also the highest (9.7 mg L^{-1}) DO values.

Electrical conductivity (EC), total dissolved solids (TDS) and total suspended solids (TSS)

The EC registers its maximum value in estuary (3720 µs cm^{-1}) and minimum in reservoir (26.91 µs cm^{-1}). The estuarine samples exhibited remarkably high EC (av. 1972 µs cm^{-1}) followed successively by well (152 µs cm^{-1}), spring (81 µs cm^{-1}), river (72 µs cm^{-1}), canals (38 µs cm^{-1}) and reservoir (31 µs cm^{-1}). In the NRB, the behaviour of TDS was similar to that of EC. The average TDS and TSS concentrations were high in the estuary (1409 mg L^{-1}; 32 mg L^{-1}) and low in the reservoir (22 mg L^{-1}; 10 mg L^{-1}).

TH and alkalinity

The average TH concentration in the different aquatic environments of NRB varied between 10 (LBC) and 188 mg L^{-1} (estuary). In river, reservoir, springs and well water samples, the average TH are 16, 11, 11 and 40 mg L^{-1} respectively. Among the different types of water sources, the estuary and well water samples recorded remarkably high TH values. Out of the six water sources of NRB, the alkalinity was the highest for wells (26.4 mg L^{-1}) and the lowest for springs (7.9 mg L^{-1}). In river, reservoir, estuary and irrigation canals the respective averages of alkalinity were 11.2, 9.4, 17.0, 11.7 (LBC) and 9.1mg L^{-1} (RBC).

Major cations (Na, K, Ca and Mg)

The estuarine environment showed higher concentrations of Na (av. 69.4 mg L^{-1}), K (av. 11.85 mg L^{-1}), Ca (av. 14.82 mg L^{-1}) and Mg (av. 36.71 mg L^{-1}) than the other water sources of NRB. The spring water samples recorded the lowest Ca (av. 1.80 mg L^{-1}) and K (av. 1.28 mg L^{-1}) concentration, at the same time LBC registered the lowest Mg (av. 1.20 mg L^{-1}) and Na (av. 2.01 mg L^{-1}) values. In the irrigation canals, the cations exhibited only marginal variation while in all the other sources the cation concentration was fluctuated considerably.

Chloride and sulphate

The chlorides and sulphates recorded the highest average values (123.67 mg L^{-1}; 67.24 mg L^{-1}) in the estuary and the lowest in well (0.59 mg L^{-1}) and reservoir (0.33 mg L^{-1}) waters. The concentration of chloride in river, reservoir, irrigation canal and springs was 11.63, 8.72, 9.89 (LBC), 8.64 (RBC) and 11.55 mg L^{-1} respectively. Of the various sub-environments examined, the samples collected from estuary showed substantially high concentration of sulphate than the other sources.

Nutrients

The average NO_3-N concentration in various aquatic environment of NRB ranged from 42.70 (reservoir) to 926.4 µg L^{-1} (river). Among the different types of water sources, the NO_3-N content was remarkably high in river (1824 µg L^{-1}) and well (1381 µg L^{-1}) water samples. The nitrate concentrations in the sub-environments were well>spring>irrigation canals> estuary. Considering the irrigation canals, the NO_3-N concentration in the RBC (av. 215 µg L^{-1}) and LBC (av. 233 µg L^{-1}) recorded only meagre variation, except for an anomalous hike at station RB6 (843.6 µg L^{-1}). The nitrite concentration also showed its highest values in river water (av. 55.4 µg L^{-1}), successively followed by estuary (av. 27.4 µg L^{-1}), reservoir (av.8.0 µg L^{-1}), irrigation canal (RBC av. 6.21 µg L^{-1} and LBC av. 5.5 µg L^{-1}) and spring (1.4 µg L^{-1}). The P_{inorg} content in the NRB varied from 215 (well) to 60.33 µg L^{-1} (spring). In the other environments like estuary, reservoir, irrigation canals and springs the averages were 168, 124, 137 (RBC), 118 (LBC) and 60.33 µg L^{-1} respectively. The average concentrations of silica were more or less similar in all the sub-environments and it varied between 3.5 (irrigation canal) and 8.4 mg L^{-1} (well).

The concentration of TC (Total carbon), IC (Inorganic carbon) and TOC (Total organic carbon) showed the highest average in well waters (av.13.65, 3.93 and 9.73 mg L^{-1}) and lowest in LBC (av. 3.75, 1.16 and 2.59 mg L^{-1}). In the other sub-environments the difference was meagre. The average concentrations of TC, IC and TOC in the various sub-environments were well>estuary>river>reservoir>irrigation canal.

Table 2 summarises the concentrations of various dissolved inorganic elements like inorganic carbon (DIC), nitrogen (DIN), phosphorous (DIP) and sulphate (DIS) transported through the Neyyar river into the receiving coastal waters. On an average, the main channel of the river contains an amount of 1.92 mg L^{-1} of DIC, 982 µg L^{-1} of DIN, 158 µg L^{-1} of DIP and 6.54 mg L^{-1} of DIS.

Table 1. Averages and ranges of various water quality parameters of the water sources/sub-environments of the Neyyar river basin in relation to water quality standards.

Parameter	River	Reservoir	Estuary	LBC	RBC	Springs	Well	WHO	BIS	ICMR
pH	6.31 (6 - 6.51)	6.50 (6.31 - 6.63)	6.26 (5.84 - 6.68)	6.63 (6.43 - 6.8)	6.21 (5.8 - 6.63)	5.26 (4.84 - 5.87)	5.9 (4.92 - 6.46)	6.5-8.5	6.5-8.5	7-8.5
EC (µS/cm)	72.37 (53.42 - 97.79)	31.287 (26.91 - 52.92)	1972.15 (224.3 - 3720)	38.08 (29.38 - 73.35)	38.02 (28.91 - 69.35)	80.67 (50 - 120)	152.36 (42.06 - 296.3)	800	800	28.14-3720
DO (mg/l)	7.48 (6.44 - 8.47)	8.063 (7.08 - 8.97)	6.4 (6.34 - 6.45)	8.9 (7.33 - 10.12)	7.35 (5.91 - 8.68)	4.56 (1.85 - 9.7)	4.01 (2.31 - 5.6)	5	5	-
Alkalinity, (mg/l)	11.27 (6 - 16)	9.4 (8 - 14)	17 (14 - 20)	11.71 (8 - 22)	9.11 (8 - 10)	7.92 (1.7 - 15.3)	26.4 (4 - 86)	20	20	-
Chloride, (mg/l)	11.63 (7.58 - 16.11)	8.719 (7.58 - 11.37)	123.67 (49.28 - 198.06)	9.89 (8.53 - 13.27)	8.64 (5.69 - 15.16)	11.55 (9.2 - 15.8)	0.59 (0.29 - 1.33)	250	250	200
Sulphate (mg/l)	6.23 (2.03 - 13.13)	0.325 (0.01 - 0.74)	67.24 (16.46 - 118.02)	2.11 (0.81 - 6.4)	2.04 (0.59 - 5.68)	1.6 (0.3 - 2.7)	15.51 (1.49 - 47.65)	200	200	200
Ca (mg/l)	3.42 (1.6 - 6.41)	2.161 (0.8 - 4.8)	14.82 (4.8 - 24.84)	2.17 (0.8 - 6.41)	2.22 (1.6 - 3.2)	1.8 (1 - 3.1)	9.13 (1.6 - 27.25)	75	75	75
Mg (mg/l)	1.9 (0.97 - 2.91)	1.261 (0.97 - 2.91)	36.71 (4.86 - 68.55)	1.2 (0.97 - 1.94)	1.94 (0.48 - 3.88)	1.28 (0.8 - 1.9)	4.27 (0.48 - 13.12)	30	30	50
Na (mg/l)	2.91 (2.5 - 3.1)	2.06 (1.1 - 2.9)	69.4 (19 - 119.8)	2.01 (1.1 - 2.8)	2.13 (1.2 - 2.8)	5.6 (4.1 - 9)	7.38 (2.7 - 18.8)	-	-	-
K (mg/l)	1.37 (0.5 - 2.5)	0.3 (0.2 - 0.5)	11.85 (1.5 - 22.2)	0.37 (0.2 - 0.5)	0.41 (0.1 - 0.9)	1.28 (0.8 - 1.7)	1.7 (0.3 - 5.5)	-	-	-
TH (mg/l)	16.36 (10 - 24)	10.6 (6 - 16)	188 (32 - 344)	10 (6 - 20)	13.56 (8 - 20)	10.65 (4 - 19)	40.4 (8 - 88)	200	300	300
NO_2-N (µg/l)	55.42 (0 - 188.01)	7.99 (0 - 79.9)	27.37 (11.62 - 43.12)	5.5 (1.97 - 12.82)	6.21 (0 - 34.19)	1.39 (0 - 5.15)	-	-	-	-
NO_3-N (µg/l)	926.4 (149.41 - 1827.42)	42.707 (3.25 - 174.71)	147.29 (110.25 - 184.32)	232.67 (8.34 - 479.47)	215.03 (10.53 - 843.6)	580 (218 - 801)	613.13 (144.68 - 1381.61)	-	-	-
P_{-inorg} (µg/l)	159.51 (136.14 - 176.84)	123.985 (59.97 - 159.39)	167.57 (152.67 - 182.47)	118.21 (99.59 - 137.03)	137.44 (109.59 - 171.57)	60.33 (51 - 73)	215.45 (140.85 - 339.69)	-	-	-
SiO_2^{3-} (mg/l)	4.65 (3.56 - 5.55)	3.968 (3.1 - 7.21)	5.36 (4.71 - 6.01)	3.5 (2.81 - 5.21)	4.02 (3.26 - 5.19)	5.25 (2.8 - 7)	8.39 (4.05 - 16.39)	-	10	-
TSS, (mg/l)	47.24 (1.2 - 109.2)	10.48 (4 - 32)	32.2 (25.2 - 39.2)	25.89 (6.4 - 42.4)	14.31 (4.4 - 34.8)	-	0.01 (0.01 - 0.02)	-	-	-
TDS, (mg/l)	51.69 (38.15 - 69.85)	22.345 (19.22 - 37.8)	1409 (160.2 - 2657.1)	27.2 (20.98 - 52.39)	27.16 (20.65 - 49.53)	48.28 (29.7 - 72)	108.83 (30.04 - 211.64)	500	500	500

Table 2. The concentration of nutrients in various water sources/sub-environments of the Neyyar river basin.

Parameter	River	Reservoir	Estuary	LBC	RBC	Well
TC	5.73 (4.78-6.34)	4.43 (3.35-5.48)	7.34	4.92 (3.55-7.27)	3.75 (3.53-3.98)	13.65 (3.94-23.37)
IC	1.89 (1.44-2.32)	1.18 (0.76-1.56)	2.03	1.18 (0.81-1.69)	1.16 (1.06-1.26)	3.93 (3.52-4.34)
TOC	3.84 (3.34-4.15)	3.16 (2.59-3.92)	5.31	3.74 (2.51-5.58)	2.59 (2.47-2.7)	9.73 (0.42-19.0)
DIN	982 (149-1876)	51 (3-255)	174.5 (122-227)	236 (8-482)	221 (11-878)	613 (145-1382)
DIP	158 (136-177)	124 (60-159)	167.5 (153-182)	118 (100-137)	137 (110-172)	215 (141-340)
DIS	6.54 (2.03-13.1)	0.33 (0.01-0.74)	67.24 (16.5-188)	2.1 (0.81-6.4)	2.04 (0.59-5.68)	16 (1.5-47.6)
DIC	1.92 (1.4-2.3)	1.32 (1.21-1.42)	1.16 (0.76-1.56)	1.18 (0.81-1.69)	1.16 (1.06-1.26)	3.93 (3.52-4.34)

The DIC, DIN, DIP and DIS in the estuarine environment are 1.16, 175, 168 and 67.24 mg L^{-1}, and reservoir environments are1.32, 51, 124 and 0.33 mg L^{-1} respectively. The concentration of dissolved nutrients in LBC and RBC are 1.18 and 1.16 mg L^{-1} of DIC, 236 and 221 µg L^{-1} of DIN, 118 and 137 µg L^{-1} of DIP and 2.1 and 2.04 mg L^{-1} of DIS, respectively.

DISCUSSION

Natural and anthropogenic determinants

Water entering in a river environment is generally from three major sources such as surface run-off, through flow and interflow, and base flow (Walling, 1980; Petts and Forster, 1985). River water is generally a dilute aqueous solution whose chemical qualities are acquired from atmospheric, soil and rock sources. The major natural sources of chemical constituents in

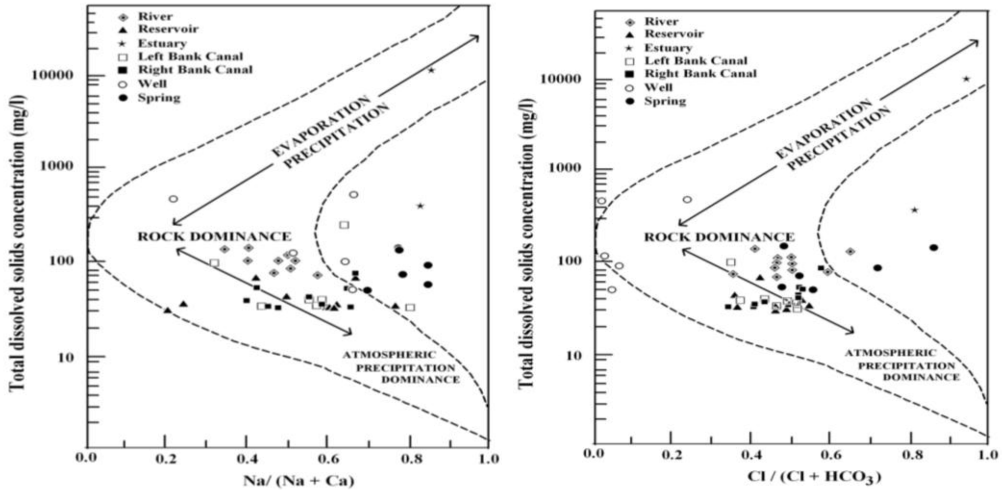

Figure 3. Plots of total dissolved solids (TDS) against Na /(Na + Ca) and Cl /(Cl + HCO3); after Gibbs (1970).

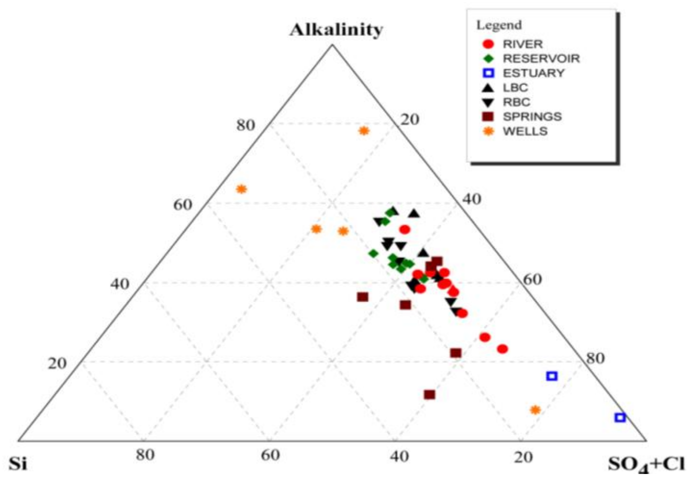

Figure 4. Stallard diagram showing the ternary plots of Si, Alkalinity and SO_4+Cl systaem.

Neyyar are precipitation and weathering. Increase in population, urbanization and industrialization has also contributed to significant changes in the quality of surface water and subsurface water sources (Krishnakumar, 2002).

Weathering of crustal rocks and leaching of soil are the major natural processes that determine the hydrochemistry of NRB. In the highlands the natural contribution of ionic constituents are considerably less because of the low residence time of surface runoff resulted from the high gradient terrain (Padmalal et al., 2011; Maya et al., 2007). But the scenario is different in the midlands and lowlands where, residence time of water is substantially high because of the low gradience of the terrain. As seen from the Gibbs diagram, atmospheric precipitations also have a significant role in controlling the chemical behaviour of the Neyyar waters in addition to rock weathering. The plots of Na/(Na+Ca) and Cl/(Cl+HCO_3) against the total dissolved solids (TDS) reveal a marked clustering in an area close to the field of rock weathering compared to the precipitation sector (Figure 3). The spread of the plots, especially the Na/(Na+Ca) against TDS is attributed to difference in the availability of these cations in the various water sources/sub-environments of NRB. The Stallard model worked out for the water samples of different environmental settings revealed that the points are segregated close to the SO_4+Cl alkalinity field, especially in the middle (Figure 4). This points to the significant role of rock weathering in regulating the water chemistry of the river, although precipitation is also a potential factor contributing the changes.

The fluctuating trend of sulphate along the river may be due to anthropogenic activities like sand mining and also the presence of soaps and detergents originated from washing and bathing activities. The increased use of chemical fertilizers in the agricultural lands is the major source N and P to the river system. The downstream reach of RBC and LBC of the NIP shows high conductivity and hardness which may be attributed to increased anthropogenic activities (sewage, industries etc.) in the area. The nutrients like N and P in the study area show wide regional as well as spatial variations. Table 3 depicts a comparative evaluation of the hydrochemical parameters of the NRB with that of some important rivers of India as well as the world river average. The pH of NRB and the other small mountainous rivers such as Manimala and Bharathapuzha rivers are acidic compared to the other major Indian rivers. Except chloride, all the other chemical parameters in general showed lower values compared to the other major rivers of India like Indus, Ganges and Brahmaputra and also the Indian and world river averages (Table 3). This might be attributed to geologic, physiographic and climatic factors of the study area. From geological setting of the area, it is evident that the NRB is composed mainly of silicate rocks whose weathering can contribute only low contents of anions and cations to the water sources. Further, the high gradient terrain over which these mountainous rivers drain can offer low residence time to the river water, which automatically limit free exchange of ions between the water and the weathered bed rocks. Another significant point is that a major part of this 56 km long river in its upstream is draining through protected a forest which is free from human interventions. All these, in one way or the other are responsible for the lower ionic averages for the Kerala Rivers including Neyyar river. However, the observed variations noticed in the case of chloride might be resulted from anthropogenic contributions from urban and agricultural (rock salt is applied for coconut trees as a soil conditioner) areas, a feature also observed earlier by Arun (2007) for the Karamana river, which drains through the northern boundary of the NRB.

Water quality assessment

Table 1 shows a comparative evaluation of the water quality parameters of study area with that of World Health Organisation (WHO), Bureau of Indian Standards (BIS) and Indian Council for Medical Research (ICMR). Except pH and DO of some of the samples, all the other water quality parameters of the NRB are in agreement with the standards set for drinking water by various agencies. The higher values of DO obtained at the downstream area may be attributed to saline water intrusion. Compared to Neyyar reservoir and canal system, the river water showed slightly higher values for all the parameters except for pH and dissolved oxygen. The water quality of the different water bodies of NRB falls within the low salinity hazard- low sodium hazard facies. This indicates the suitability of the water for irrigation purposes (Figure 5).

The chemical quality of water collected from the RBC is almost agreeable with drinking water standards, but little correction required in the case of pH. The average pH of RBC is less than the standard set by WHO. According to the Central Pollution Control Board, Government of India classification, water samples collected from wells namely Aruvikkara (well no.2), Ulloorkonam (Well No.4) and Balaramapuram (Well No.5) fall in the category ‘C’ which is good for drinking only after convectional treatment and disinfection (Table 4).

Dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), dissolved inorganic carbon (DIC) and sulphate

Rivers are the major contributors of dissolved materials into the ocean realms. It is estimated that the world's major rivers transport an amount of 12-13x10^9 tonnes of dissolved materials into the oceans annually (Milliman and Meade, 1983). Among the dissolved components, the inorganic forms of nutrients received considerable significance in recent years, as they have a strong bearing on the productivity of the aquatic environments. Although many studies on dissolved nutrient transport are available for the major rivers, studies on small rivers having catchment area <10000 km^2 are scarce.

All the measured water quality parameters are substantially low in the Neyyar reservoir (Table 1). The parameters exhibit a marked increase in the main channel of the river. The sulphate concentration shows an exponential rise towards the estuarine region. With the exception of DIP, all the other parameters exhibit an increase in the midlands. The DIP, on the other hand, exhibits a highly fluctuating trend along the profile of the river. The distribution of these geochemical signals in the Neyyar is function of the intensity of weathering as well as sedimentary and biologic processes operating in this fluvial system. High degrees of human interventions like agricultural activities, indiscriminate sand mining, etc., are the major factors for the observed anomalous hike of these parameters in the midland reaches of the river. A time series analysis carried out for the dissolved sulphate using the previously published data of Thrivikramji (1986) and Krishnakumar (2002) reveals that the concentration of sulphate exhibits an increasing trend over the past 25 to 30 years. Oxidation of iron sulfide minerals in the sub-surface organic matter rich interlayers exposed during pit excavation for sand is one of the major causative factors enhancing the content of sulphate in the overlying waters of the Neyyar. A similar observation is

Table 3. Comparative evaluation of average chemical composition of the Neyyar river with that of some of the important Kerala rivers (Serial Nos 2-3), Indian major rivers (4-7), Indian average and world averages.

S/N	River/River average	P^H	Concentration (mgl^{-1})									Reference
			Ca	Mg	Na	K	HCO_3	Sulphate	Chloride	SiO_2	TDS	
1	Neyyar river[(a)]	6.31	3.42	1.9	2.91	1.37	11.27	6.23	11.63	4.65	51.69	Present study
2	Manimala river[(a)]	6.56	2.63	1.24	2.76	1.57	8.73	4.16	9.26	-	28.62	Padmalal et al. (2010)
3	Bharathapuzha river[(a)]	6.46	8.88	3.55	3.69	1.41	21.1	10.05	15.80	9.08	68.60	Babu et al. (2003)
4	Ganges	7.30	16.90	12.80	18.40	5.90	170.50	17.19	14.00	26.4	281.0	Subramanian (1979)
5	Brahmaputra	-	14.00	3.80	2.10	1.90	58.00	10.00	11.00	7.80	100.0	Subramanian (2000)
6	Indus	7.70	28.80	0.72	1.25	2.10	64.00	15.00	9.20	5.30	124.0	Subramanian (1979)
7	Indian Rivers (average)	7.70	23.08	6.29	3.73	2.32	90.77	11.38	6.28	14.7	159.0	Subramanian (1979)
8	World Rivers (average)	6.10	15.00	4.10	6.30	2.30	58.40	11.20	7.80	13.1	120.0	Livingstone (1963)

(a) Non Monsoon period; All others are annual average values.

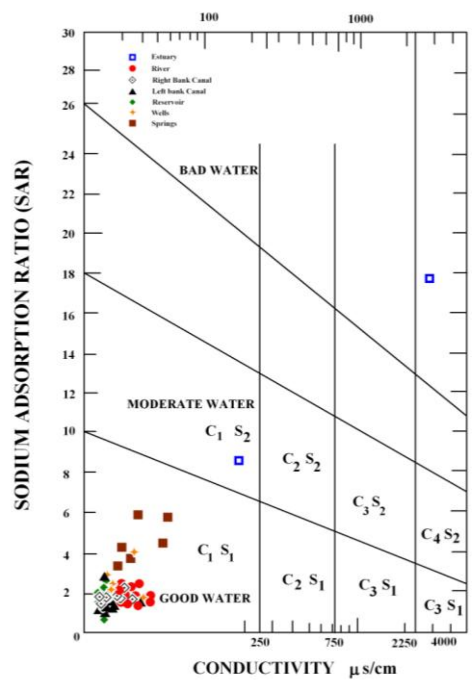

Figure 5. Classification of various water sources of Neyyar river basin based on EC and SAR; after Richard (1954).

Table 4. Classification of water types, Central Pollution Control Board, Government of India.

characteristics	CPCB standards				
	A	B	C	D	E
DO (mg/l)	6	5	4	4	-
BOD (mg/l)	2	3	3	-	-
Total coliforms (MPN/100ml)	50	500	5000	-	-
TDS (mg/l)	500	-	1500	-	2500
Chlorides					
Colour (hazen units)	10	300	300	-	-
sulphates	400	-	400	-	1000
nitrates	20	-	50	-	-
pH	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5	6.5-8.5
conductivity	-	-	-	1.0	2.25

A- Drinking water source without conventional treatment but after disinfection; B- Outdoor bathing organized; C- Drinking water source with conventional treatment followed by disinfection; D- Propagation of wildlife and fisheries; E- Irrigation, industrial cooling, controlled waste disposal.

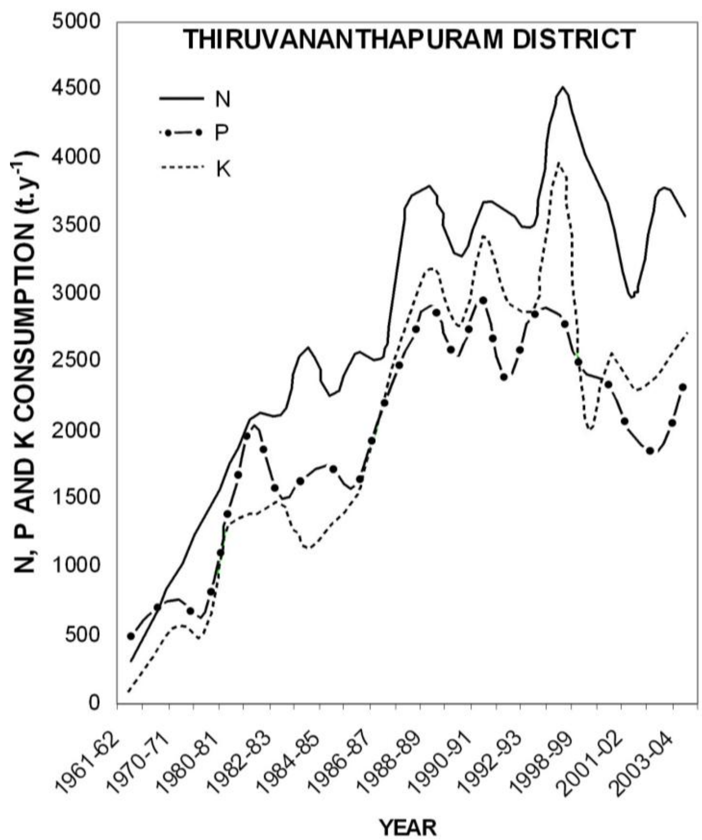

Figure 6. Quantity of nitrogen (N), potassium (K) and phosphorus (P) fertilizer consumption in Thiruvananthapuram district during the period 1961/62 to 2003/04 (Source: Agricultural Department, Government of Kerala).

reported earlier from the Manimala river by Padmalal et al. (2011).

The fertilizer intensive agricultural activities are, perhaps, the major sources of DIN and DIP in the study area.

Conclusions

The Neyyar is a small, perennial river with a length of 56 km and catchment area of 497 km^2. Apart from the fluvial channels, the Neyyar River Basin (NRB) hosts many fresh water sources- wells, springs, irrigation canals and a reservoir. The basin area experiences severe drinking water scarcity in summer season (January to May) every year. Further, anthropogenic activities impose marked water quality problems in the area. The present study on the chemical quality of water in various surface and subsurface water sources of NRB reveals that with the exception of pH and DO in certain samples, all the other water quality parameters are well within the water quality standards set by WHO and BIS. The plots of Na/(Na+Ca) and Cl/(Cl+HCO_3) against total dissolved solids are clustered around the field of rock weathering. This clearly indicates chemical alteration of the geological formation/ rock types in regulating the ionic gradients of the water sources. At the same time, the sulphate and nutrients like N and P are resulted mainly from the anthropogenic sources. The fertilizer intensive agricultural activities are perhaps the major source of dissolved N and P in the surface and subsurface waters of the study area. The study reiterates the need for stringent mitigation measures to regulate adverse impacts of human interventions in the NRB as well as the other small catchment rivers in the region as these rivers are more responsive to anthropogenic interferences.

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