



Distribution of Major Ions in Ground Water, River Water and Estimation of Ground Water Recharge in Mulki River Basin, South-West Coast of India

MINAL GUNE¹, K BALAKRISHNA¹, H N UDAYASHANKAR¹ AND B R MANJUNATHA²

¹Department of Civil Engineering, Manipal Institute of Technology, Manipal University, Manipal 576104, India

²Department of Marine Geology, Mangalore University, Mangalagangothri 574199, India

Email: k.balakrishna@manipal.edu

Abstract: This study focuses on the seasonal variations in ground water, river water chemistry and estimation of ground water budgeting using chloride mass balance method around Mulki River basin. Chloride ion is used as a tracer due to its conservative nature, thus making it easier for estimation of ground water budgeting as well as to assess the sources in river and ground water of Mulki River basin. The seasonal variability of major ions, Na/Cl ratio in ground water and river water revealed that, the dissolution of Ca-bearing silicate rocks and atmospheric inputs are the major sources vis-à-vis anthropogenic sources. The annual ground water recharge estimation reveals that the mean ground water recharge (272mm/year) is lower than the mean river water discharge (58 m³/s) and annual rainfall (3763 mm). This decrease in the ground water recharge may be due to the impact of evapotranspiration (1466 mm/year), high discharge in to the river due to steep slope and the presence of granitic terrain that possess less porosity and are of impermeable nature. This method is found to be suitable for ground water budgeting in places where there are less number of rain gauge stations on river basins in India. This baseline study would be very helpful for ground water modelling and water resource management. This work could be the first report on the seasonal variability of major ions, their source determination using chloride ion as a tracer in ground water, river water and also water budgeting using chloride mass balance technique in Mulki River basin Southwest coast of India.

Keywords: Major ion concentration, seasonal variations, principal component analysis, chloride mass balance, thematic mapping

1. Introduction

Increased population, rapid growth of industries, urban infrastructure has resulted in increased requirement of water resources and also need to assess its quality. Ground water and river water plays a major role in domestic, irrigational and industrial purposes in India. Due to increasing demand, decreasing availability of surface water resources as a result of high evapotranspiration and runoff, particularly in non-monsoon seasons, people are now relying more on ground water resources. There is an increased demand for ground water resources in Udupi, Dakshina Kannada districts due to a surge in industrialization and development in recent times. This has also resulted in contamination of surface water due to industrial effluents along with excessive withdrawal of ground water [1]. In general, quality of ground water and river water is affected by several factors like atmospheric inputs, climate, geology, hydrological flow, anthropogenic influence [2]. Therefore, it is essential to monitor the hydro-geochemistry of river, ground water, its recharge estimation for ground water modelling and water resource management. Chloride ion is used as a tracer for recharge estimation and source identification due to its conservative nature. The ion possesses non-absorbent and non-percolating nature in aquifers. The

above characteristic feature helps to identify the sources and to estimate the ground water recharge. This paper delineates the sources including natural, anthropogenic that affect the river water, ground water chemistry and its budgeting using chloride ion as a tracer in Mulki River basin south-west coast of India. This baseline study is very helpful to understand the hydro geochemistry of river, ground water, predicting the recharge of ground water and discharge from the river water.

1.1 Study area

Mulki River originates on the foothills of Western Ghats and flows westerly into the Arabian Sea. The river basin was found to be rectilinear in shape. The river possessed a length of ~ 75 Km² and basin surface area of ~ 578.8 Km². Mulki River basin lies in close proximity to an agricultural land near Mulki town (Fig 1). It is located between 13° 0' N, 13° 15' N latitudes, 74° 45' E and 75° 0' E longitude [3]. It is surrounded by Padubidri to the North, Karkala to the east, Surathkal to the south and Arabian Sea to the west.

The study area has a typical tropical climate, with an annual average temperature and rainfall of 26° C and 3763 mm respectively [4]. The area experiences moderately dry weather during winter (November to

January) compared to early summer (February to May) [5]. The annual discharge from the river basin is $58 \text{ m}^3/\text{s}$, annual evapotranspiration is 1466 mm as shown in Figure 2 and annual precipitation is 3763 mm (data from India Meteorological Department, Government of India, <http://www.imd.gov.in>) [6].

Geology of the study area belongs to the Archean Era. The river catchment area is made up of granitic gneisses, laterites and riverine sands [3]. The

geological formations are mainly crystalline rock consisting of granite gneiss covered by relatively thick regolith of lateritic and sandy soils. These rocks are tropically weathered to laterites and are covered with sandy and red lateritic soils. The sandy soils are fine to medium textured, which are observed more towards the coastal track, whereas the lateritic soils are coarse to fine textured and are observed in the hinterland region [7].

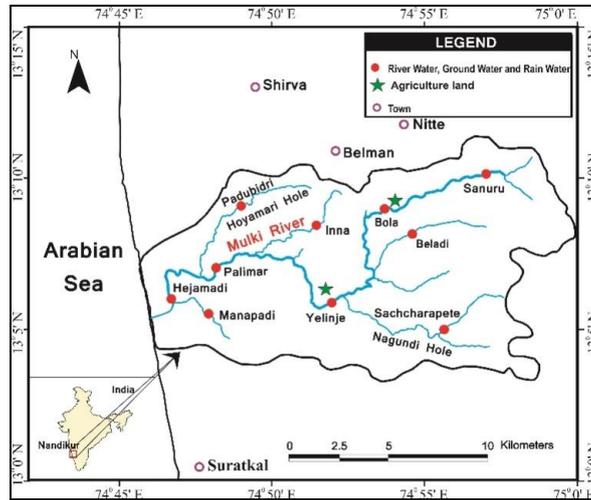


Figure 1: Map showing the basin of Mulki River and location of sample stations

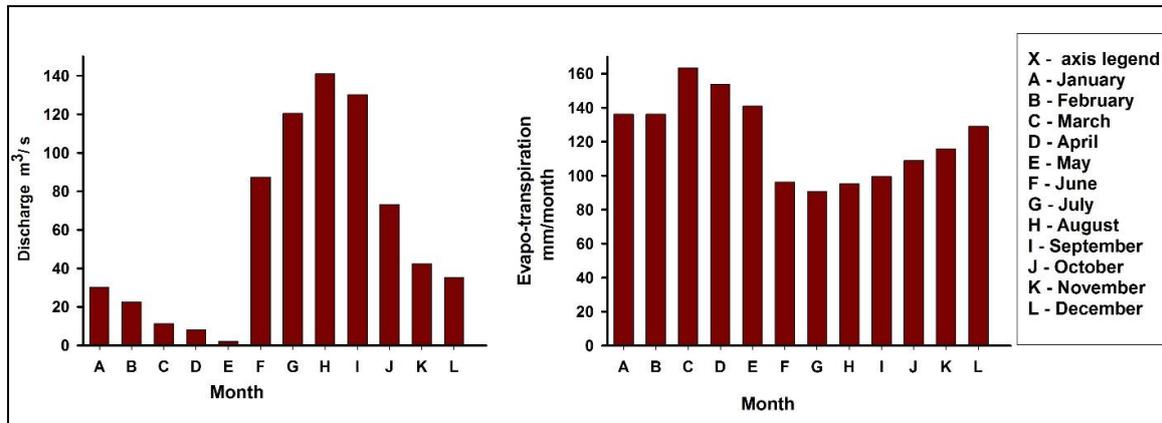


Figure 2: Annual river water discharge and evapo-transpiration data of Mulki River basin

1.2 Methodology

The river, ground water samples were collected during pre-monsoon (March), early-monsoon (June), monsoon (September) and post-monsoon (December) period i.e., from December 2012 to December 2013. The water samples were collected from ten locations at the river channel which includes upstream at Sanuru, Beladi, Bola, Sachcharapete, mid-stream at Yelinje, Inna, Palimar and down-stream at Manapadi, Padubidri, Hejamadi (Fig 1). Water sampling has been done at the center of river channel. The ten ground water samples/ season (4) were collected from open wells using polythene bucket tied with a nylon rope, so as to avoid any metal contamination. Rain water sampling was carried out on a monthly basis in the same stations as mentioned above in river water

samples. The rain water samples were collected to estimate the ground water recharge and identify the sources using chloride ion as a tracer. The rain water sample collection at the same station, as mentioned above in the river water samples were set-up at an elevation of $\sim 40 \text{ m}$ above the ground level in order to avoid the influence of local sources. Narrow mouth carboy attached with funnel was used for rain water collection. The funnel was covered with a plastic mesh to avoid contamination from solid and plant particles. The physico-chemical parameters like temperature ($T^\circ\text{C}$), pH, electrical conductivity ($\text{EC } \mu\text{S cm}^{-1}$) and TDS (total dissolved solids, mg/l) measurement have been carried out simultaneously. These parameters measurements have been done using pre-calibrated Hach make multi-parameter

instrument. The water sampling has been done in pre-cleaned one liter polypropylene (PP) bottles. The PP bottles were rinsed with the sample to avoid dilution and contamination. The bottles were placed in polythene bag and transported to laboratory for additional processing and extraction. The collected water samples were filtered using cellulose acetate filter paper (0.22 μm pore size and 47 mm diameter), through a filtration unit (Sartorius make) operated by a hand vacuum pump (Mityvac). Filtration has been done in a laminar flow bench on the same day.

The first 25 ml of filtered samples was rejected and an additional 100 ml was used for washing pre-cleaned PP bottles prior to preserving samples for geochemical analysis. The next batch of filtered water samples were poured in 125 ml PP bottles for major ions analyses and were preserved at 4 $^{\circ}$ C until analysis [8]. The filtered water samples were measured for bicarbonate concentration by acid titration (0.02 N hydrochloric acid) using an autotitrator (Metrohm make model-Tiamo 888). Silica in water samples was measured using Hach make UV-Vis spectrophotometer. Major ions were analyzed using Ion chromatography (Dionex make -1100) fitted with the auto sampler. The accuracy of the water analysis was checked with cation and anion balance. The charge balance varies within $\pm 20\%$. Few rain water samples have shown higher charge balance [9,10].

1.3 Results and Discussion

1.3.1 Physico-Chemical Parameters

The chemical properties of Mulki River water were studied for a period of one year, i.e., from December 2012 to December 2013 covering pre-monsoon, early-monsoon, monsoon and post-monsoon seasons. pH concentration in monsoon season was found to be mildly acidic in ground water and river water. It indicates that the impact of heavy rain which causes dilution in concentration. In ground water and river water during pre-monsoon, early-monsoon and post-monsoon season, pH concentration ranges from acidic to alkaline nature, along with high TDS and conductivity as shown in Table 1.1 and 1.2. It

suggests the influence of silicate rock and sea salt from Arabian Sea. The alkalinity was found to be low in monsoon, post-monsoon season compared to pre-monsoon and early-monsoon season in river water and early-monsoon season in ground water. It indicates that the impact of heavy rain causes dilution in concentration. In pre-monsoon season, ground water samples showed low alkalinity compared to early-monsoon and post-monsoon season. Temperature varies from 25 to 27 $^{\circ}$ C during wet period and 29 to 31 $^{\circ}$ C during dry period.

1.3.2 Seasonal variations in major ion concentration

Na $^{+}$ and Cl $^{-}$ ion shows low concentration during monsoon season in ground water (7.79 and 7.88 mg/l) and river water (7.36 and 3.96 mg/l) compared to pre-monsoon, early-monsoon and post-monsoon seasons. It reflects the influence of monsoonal rains, which causes dilution in concentration (Table 1.1 and 1.2). Their concentrations are higher in rest of the seasons, which could be because of sea salt from Arabian Sea and anthropogenic activity. Ca $^{2+}$, Mg $^{2+}$, K $^{+}$ and Silica shows high concentration in river and ground water during pre-monsoon, early-monsoon season compared to monsoon and post-monsoon season. The low concentration of Ca $^{2+}$, Mg $^{2+}$, K $^{+}$ and Silica in river and ground water during monsoon and post-monsoon season, indicates the dilution by monsoonal rains [11]. In pre-monsoon season NO $_3^{-}$ and SO $_4^{2-}$ shows higher concentration in ground water (2.1, 2.3 mg/l) compared to early-monsoon, monsoon and post-monsoon season. It reflects the influence of anthropogenic activity like percolation of domestic sewage from septic tank and leaching of fertilizers from agricultural land near Mulki. In river water during early-monsoon, monsoon and post-monsoon season NO $_3^{-}$ concentration (0.32, 0.37, 0.67 mg/l) was higher than pre-monsoon season (0.31 mg/l). The SO $_4^{2-}$ concentrations were high during monsoon (0.95 mg/l), early-monsoon (0.72 mg/l) season than post-monsoon (0.40 mg/l) and pre-monsoon (0.56 mg/l) season.

Table 1.1: Physicochemical and major ion concentration of ground water (Na $^{+}$, K $^{+}$, Mg $^{2+}$, Ca $^{2+}$, Cl $^{-}$, NO $_3^{-}$, SO $_4^{2-}$, Alkalinity, Silica, TDS are present in mg/l, Temperature - T $^{\circ}$ and Conductivity in $\mu\text{s}/\text{cm}$)

Major ion concentration	Pre-monsoon ground water				Early- monsoon ground water			
	Min	Max	Sum	Average	Min	Max	Sum	Average
Na $^{+}$	2.624	18.78	93.08	9.308	2.934	41.39	113.8	11.38
K $^{+}$	0.005	11.88	35.16	3.516	1.747	12.19	46.56	4.656
Mg $^{2+}$	0.519	7.723	33.35	3.335	1.964	6.680	40.69	4.069
Ca $^{2+}$	3.192	43.41	123.1	12.31	3.088	9.818	55.42	5.542
Cl $^{-}$	4.645	20.36	120.7	12.07	6.131	10.89	83.81	8.381
NO $_3^{-}$	0.001	8.753	20.88	2.088	0.078	1.942	7.301	0.730
SO $_4^{2-}$	0.001	10.06	23.01	2.301	0.007	2.009	8.768	0.876
Alkalinity	0.305	79.61	456.4	45.64	8.27	101	616.6	61.66
pH	6.25	7.56	70.8	7.08	6.03	7.05	65.86	6.586
Conductivity	87	303	1666	166.6	83	198	1368	136.8

Silica	170	350	2439	243.9	95	325	2260	226
TDS	55.7	194	1061	106.1	53.1	127	875.6	87.56
Temperature	26.4	29	281.5	28.15	23.4	29.4	281.4	28.14
Monsoon ground water				Post- monsoon ground water				
Na⁺	4.211	15.87	77.81	7.781	4.109	41.39	125.6	12.56
K⁺	1.522	12.18	37.56	3.756	1.072	3.139	15.99	1.599
Mg²⁺	1.491	6.522	33.69	3.369	0.891	4.681	22.52	2.255
Ca²⁺	2.351	9.818	43.43	4.343	1.277	7.440	48.11	4.811
Cl⁻	6.130	9.976	78.83	7.883	5.103	29.98	115.1	11.51
NO₃⁻	0.078	1.942	7.358	0.735	0.159	2.572	10.36	1.036
SO₄²⁻	0.196	1.590	9.468	0.946	0.003	2.008	4.634	0.463
Alkalinity	26.57	79.3	456.07	45.61	17.93	115.9	557	55.7
pH	5.07	6.15	54.42	5.442	6.45	7.9	71.95	7.195
Conductivity	35	127	799	79.9	77	208	1337	133.7
Silica	133	275	2092	209.2	155	300	2224	222.4
TDS	22.4	51.12	511.2	51.12	49.3	133	855.8	85.58
Temperature	26.1	28	270.6	27.06	26	28.1	271.5	27.15

It reflects the impact of agricultural fertilizers. During post-monsoon season, fertilizers like copper sulphate and ammonium carbonate are sprayed to the arecanut and paddy fields to avoid moistness in seeding, which might contribute to the sulphates in ground water and river water [9]. This is asserted by principal component analysis, discussed in section 1.3.6. Overall river water samples shows low concentration of major ions compared to ground water. This suggests that the influence of heavy rainfall and high discharge leads to more dilution in the river water. This is also confirmed by ground water recharge estimation discussed in section 1.3.5.

1.3.3 Ionic ratio: Na/Cl

The Na/Cl molar ratio helps us to identify the process that controls the salinity, to understand the impact of natural, anthropogenic activity in rivers and ground water. The Na/Cl ratio of marine water is 0.85 [12]. If the Na/Cl ratio is ~0.85 in rivers, ground water samples, it indicates that the samples are more influenced by marine water and conversely, if the ratio is <0.85, it indicates the influence of

anthropogenic activities. In the study area the Na/Cl ratio of river water and ground water samples is 3.1 and 1.74 respectively, which is higher than the ratio of marine water 0.85. It implies that the samples are more influenced by natural sources like sea salt from the Arabian Sea and weathering of basement rocks [4] (Fig 3). A very few samples show low concentration of Na/Cl ratio compared to marine water, such as Hejamadi, Beladi in pre-monsoon season, Sachcharapete in pre-monsoon, early-monsoon, post-monsoon season in ground water and Sanuru in river water samples during early-monsoon, pre-monsoon season.

1.3.4 Seasonal variations in chloride ion concentration in ground water and river water

The chloride (Cl⁻) ion is used as a proxy for ground water budgeting, source identification in river and ground water [13, 10]. The chloride ion shows seasonal variability in ground water and river water as depicted in Figure 4. Ground water and river water samples showed high concentration of Cl⁻ ion in all seasons when compared to rain water.

Table 1.2: Physicochemical and major ion concentration of river water (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻, Alkalinity, Silica, TDS are present in mg/l, Temperature - T⁰ and Conductivity in μ s/cm)

Major ion concentration	Pre-monsoon River water				Early-monsoon River water			
	Min	Max	Sum	Average	Min	Max	Sum	Average
Na⁺	0.005	17.72	75.75	7.575	0.005	15.18	72.37	7.237
K⁺	1.266	4.393	22.43	2.243	0.807	5.263	26.38	2.638
Mg²⁺	1.228	4.779	27.10	2.710	1.127	5.513	27.45	2.745
Ca²⁺	2.644	10.82	55.76	5.576	2.923	9.059	50.67	5.067
Cl⁻	1.758	11.16	56.65	5.665	1.078	10.87	53.22	5.322
NO₃⁻	0.064	1.019	3.154	0.315	0.001	1.019	3.192	0.319
SO₄²⁻	0.007	1.039	5.576	0.557	0.048	2.181	7.203	0.720
Alkalinity	26.55	73.40	469	46.9	28.22	67.22	458	45.8
pH	6.45	7.33	68.05	6.805	6.01	7.33	66.06	6.606
Conductivity	38.3	105	618.5	61.85	43.40	76.1	596.3	59.63
Silica	73	141	1028	102.8	78	145	1103	110.3
TDS	24.5	48	360.9	36.09	38.3	68	546.5	54.65

Temperature	23.4	29.4	282.2	28.22	26	28.1	270.4	27.04
Monsoon River water				Post-monsoon River water				
Na ⁺	4.253	15.96	73.50	7.350	4.223	20.88	94.93	9.493
K ⁺	0.572	5.522	18.23	1.823	0.160	5.522	16.05	1.605
Mg ²⁺	1.273	3.54	18.91	1.891	0.013	3.369	9.901	0.990
Ca ²⁺	2.365	24.35	55.57	5.557	0.127	24.35	40.89	4.089
Cl ⁻	1.173	13.27	39.58	3.958	1.369	6.121	39.68	3.968
NO ₃ ⁻	0.003	1.27	3.713	0.371	0.003	2.39	6.782	0.678
SO ₄ ²⁻	0.002	3.284	9.522	0.952	0.001	1.569	4.011	0.401
Alkalinity	11.77	85.18	369	36.9	7.93	66.67	316.1	31.61
pH	5.07	6.15	54.42	5.442	5.21	6.33	58.97	5.897
Conductivity	21.9	55.6	379.8	37.98	38.3	68	546.5	54.65
Silica	63	126	864.8	86.48	70	130	961	96.1
TDS	14	35.6	242.7	24.27	24.5	43.5	349.4	34.94
Temperature	25	26.7	259.3	25.93	25	26.7	258.9	25.89

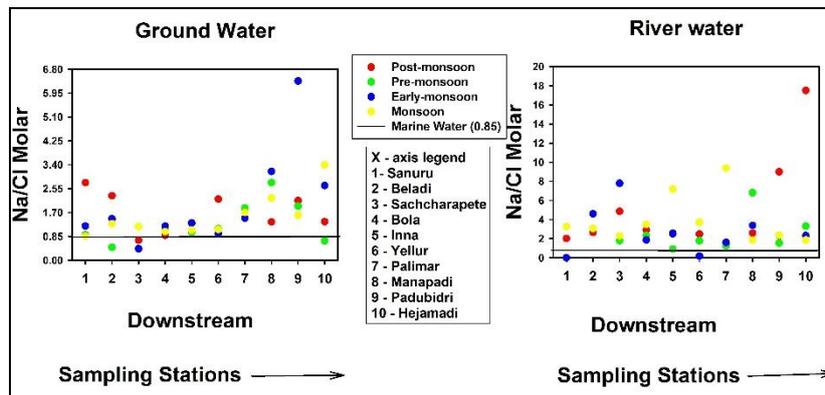


Figure 3: Scatter plot of Na/Cl (molar) for the ground water and river water in Mulki River basin

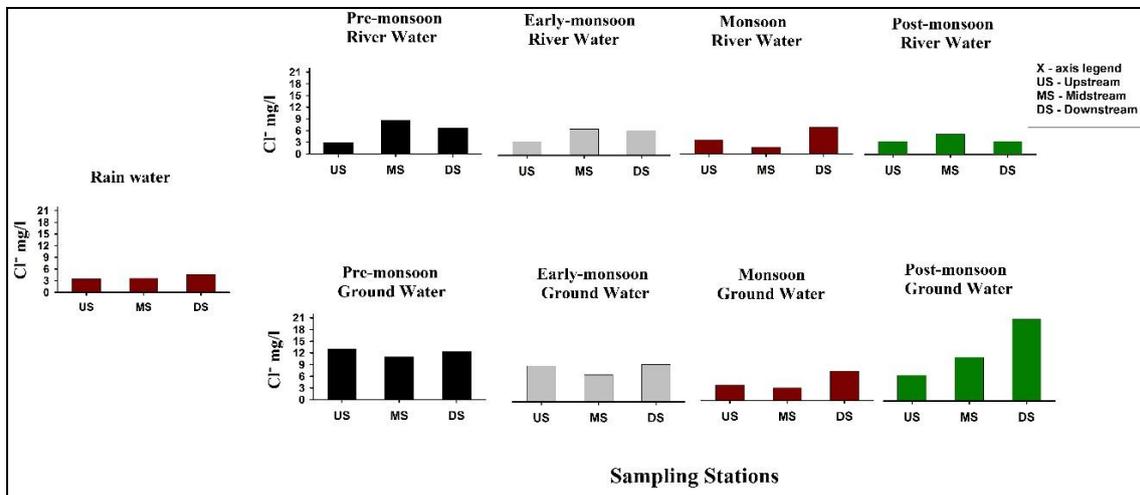


Figure 4: Seasonal variations in chloride ion concentration of ground water and river water

The higher concentrations of Cl⁻ in the river could be either from the lithology or anthropogenic sources. However, there is no presence of evaporites in the catchment and hence its contribution is negligible. Anthropogenic sources like domestic sewage from septic tank and leaching of fertilizers from agricultural land could be contributing to the excess Cl⁻. However, in the early-monsoon and monsoon season, the major sources of Cl⁻ could be from the sea salt, as reflected by similar concentrations observed in rain water (Fig 4).

The spatial distribution of chloride concentration in ground water, river water is interpolated and plotted as a thematic diagram. The thematic diagram is plotted using Arc Gis 10.2.1 which uses inverse distance weighted(IDW) system. The diagram shows the concentrations at sampling points to investigate the contamination in the region. The stations are split into zones. The river water samples in downstream and midstream shows high concentration of Cl⁻ ion compared to upstream. It suggest that the influence of sea salt from Arabian Sea and atmospheric inputs is

more towards the midstream, downstream compared to upstream as shown in Figure 5. The ground water samples in downstream and upstream shows high Cl⁻ concentration compared to midstream (except Yelinje station). It reflects the influence of natural as well as anthropogenic activity. The ground water chloride

concentration was significantly higher compared to river water (Fig 6). It indicates high discharge from river water which causes dilution in concentration [10 and 14]. This is confirmed by ground water recharge estimation as discussed in section 1.3.5.

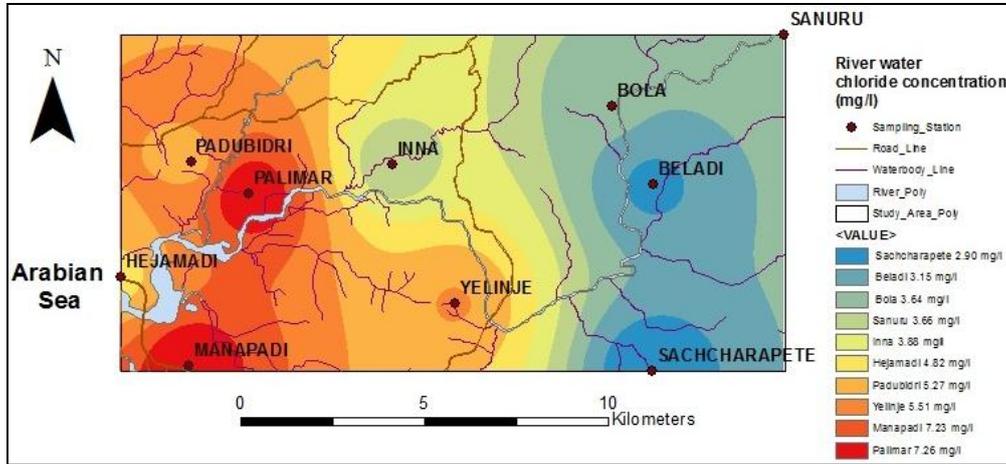


Figure 5: Thematic map representing chloride ion concentration in river water

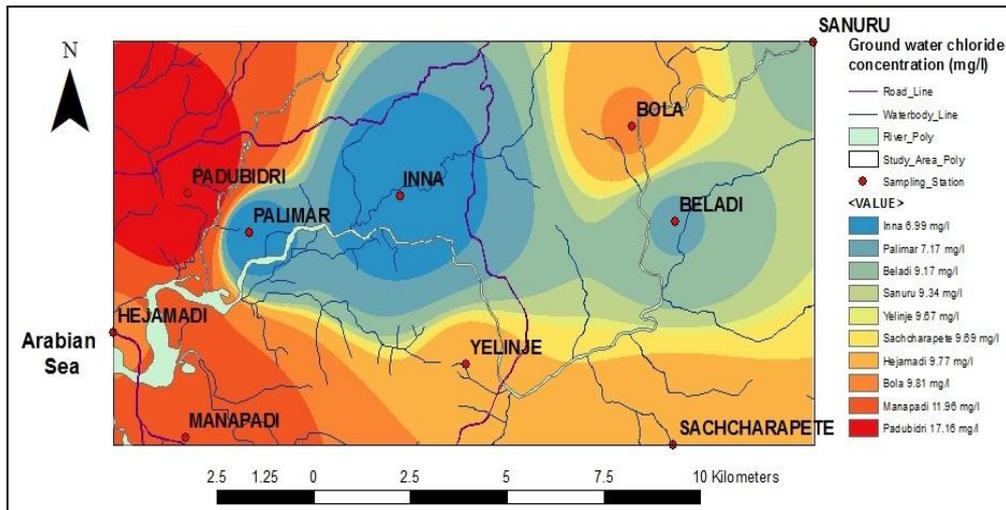


Figure 6: Thematic map representing chloride ion concentration in ground water

1.3.5 Estimation of ground water recharge

Chloride ion is used as a tracer to estimate ground water recharge in and around Mulki River basin. The ground water recharge was estimated using the following formula

$$\text{Recharge} = P \frac{Cl^-_{\text{Precipitation}}}{Cl^-_{\text{groundwater}}}$$

Where Cl⁻ is the concentration of chloride in (mg/l), P is the annual rainfall expressed in mm/year. Recharge is expressed in mm/year [15]. From ground water recharge estimation, it is observed that the mean annual discharge of river basin (58 m³/s, 54 %), was higher during the monsoon period. This is confirmed by the bed profile data collected from www.cgwb.com of Dakshina Kannada District. The

average annual evapo-transpiration obtained was 1465 mm (39%) which was particularly more during pre-monsoon (589 mm) as compared to early-monsoon (354 mm), monsoon (285 mm) and post-monsoon season (391 mm) (Fig 2). The monsoon period (June to September) shows low evapo-transpiration compared to early-monsoon, pre-monsoon and post-monsoon seasons. This could be attributed to the presence of high humidity. The ground water recharge estimation reveals that the river water discharge is higher than the ground water recharge (272 mm/year, 7 %), this may be due to the impact of high evapo-transpiration and less percolation through the rock as shown in Figure 7.

The presence of laterite terrain, which is formed as a result of granite rock weathering could be the reason for this phenomenon. Although laterite rock has more

porosity, it possesses less permeability which in turn causes low percolation. Similar behavior was obtained by Subyani [16], Vanum and Hailu [10], Bazuhair and

Wood [15], Sharda et al. 2006 [17], and Hegde 2007 [4] where the ground water recharge varied from 4 – 11 % of the average annual precipitation.

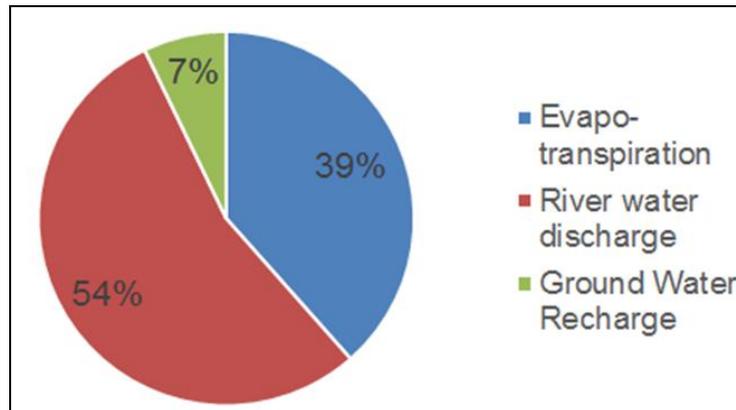


Figure 7: Annual river water discharge of Mulki River basin

Table 2: Eigen values of Major Ion concentration obtained from Principal Component Analysis

Variable	Ground water				River water			
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3	Factor 4
Na ⁺	0.749	0.152	0.372	-0.111	0.421	-0.1	0.579	0.059
K ⁺	0.029	0.434	0.733	-0.012	0.053	0.919	0.056	-0.022
Mg ²⁺	0.239	0.251	0.842	-0.116	0.364	0.586	0.176	0.055
Ca ²⁺	-0.004	0.035	-0.053	0.970	-0.048	0.839	-0.123	-0.051
Cl ⁻	0.590	0.569	-0.120	-0.047	0.319	0.462	0.441	0.291
NO ₃ ⁻	-0.158	0.915	0.062	0.026	-0.058	0.118	0.749	-0.201
Alkalinity	0.506	-0.130	0.533	0.432	0.137	0.175	-0.071	0.78
pH	-0.174	-0.207	0.732	0.027	-0.905	-0.145	-0.031	0.125
Conductivity	0.947	-0.104	-0.060	0.106	0.954	0.117	0.062	0.021
Silica	0.848	-0.132	0.153	-0.111	0.906	-0.017	0.161	0.19
TDS	0.898	-0.036	-0.136	0.150	0.926	0.13	-0.055	-0.087
SO ₄ ²⁻	-0.047	0.941	0.154	-0.002	-0.023	-0.006	0.794	-0.109
% of variance	32.563	22.711	14.988	9.82	33.422	15.331	13.525	9.305
Cumulative %	32.563	55.274	70.262	80.082	33.422	48.753	62.278	71.583

Extraction method: Principal component analysis

Rotation Method: Varimax with Kaiser Normalization

1.3.6 Principal component analysis

Major ions data in and around Mulki River basin was interpreted by R-mode factor analysis (SPSS V 21). Table 2 shows the factor scores with rotated component matrix.

The ground water samples yielded four factors. 1st factor was highly loaded with Na⁺, Cl⁻, alkalinity, conductivity, TDS and silica suggesting their source to catchment rocks. 2nd factor was loaded with Cl⁻, NO₃⁻ and SO₄²⁻ suggesting influence of both natural as well as anthropogenic activity. 3rd factor was highly loaded with K⁺, Mg²⁺, pH and alkalinity confirming the major influence of rock dissolution. 4th factor was loaded with Ca²⁺ ions indicating dissolution of Ca-bearing silicate rock which controls the concentration.

The river water samples were loaded with four factors. 1st factor was highly loaded with conductivity, silica and TDS; 2nd factor was loaded with K⁺, Mg²⁺ and Ca²⁺. Both these factors suggests the source of

these ions to the dissolution of Ca-bearing silicate rocks. 3rd factor was highly loaded with Na⁺, NO₃⁻ and SO₄²⁻ suggesting the influence of domestic sewage from septic tank, leaching of agricultural fertilizers near Mulki and dissolution of Ca-bearing silicate rock. 4th factor was weakly loaded with all major ions indicating the dissolution of ions, except alkalinity (0.78). This may be due to heavy discharge from river water.

1.4 Conclusion

Results of physico-chemical parameters, major ion chemistry and statistical analysis of Mulki River and the groundwater samples in the catchment indicate that their chemistry is controlled by the weathering of catchment silicate rocks. Minor influences of anthropogenic sources like domestic sewage and agricultural effluents (presence of nitrates and sulphates) were observed in a few groundwater (open well) samples in the pre-monsoon season when these wells had very low water and could be receiving the

effluents from the adjacent septic tanks. Presence of nitrates and sulphates were also observed in the river during the early-monsoon, monsoon and post-monsoon due to irrigation return flow. Chloride mass balance technique, which was adopted for the first time in Mulki River catchment revealed that 54% of the total rainfall in the catchment is transferred to the adjacent Arabian Sea through the riverine transport, 39% goes back to the atmosphere through the evapo-transpiration and 7% is recharged to the groundwater.

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