Anomalous SO₄-Cl groundwater in the coastal aquifer, Kerala

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Abstract. Groundwater in laterite along the northern part of the Kerala coast shows anomalous concentration of SO₄ and Cl ions. Investigation based on the chemical characteristics of groundwater, rain and Arabian seawater together with results of the laterite-water interaction experiment and sea-aquifer water-chemical mixing models show that Tertiary sediments in this region are the main source contributing SO₄ and Cl ions to the groundwater system.

Keywords. Laterite; geochemistry; laterite-water interaction; sea-aquifer model.

1. Introduction

Laterites form the major coastal aquifer of Kerala and provide drinking water to the rural population. Groundwater is extracted through open dug wells whose density varies from 250 to 300 in an area of 1 sq. km. Water available through these wells is certain road cuts. The Tertiaries invariably contain siderite and pyrite. The thickness of the laterite layer shows anomalies and sometimes make the water unpotable. Since these open wells are located near the coast, such chemical anomalies are attributed to the mixing of seawater. Seawater intrusion does occur in certain localities but it is not a common phenomenon. Earlier investigations showed that excess withdrawal of groundwater from the wells causes the levels to fall below the mean sea level, thereby creating a negative gradient and promoting the entry of seawater into the aquifer (Chandrasekharam 1985). In the area under investigation, groundwater shows large incidence of SO₄ and Cl ions relative to bicarbonate ions. It is shown here that a source other than the sea is responsible for enhancing the concentration of these ions in the groundwater.

The area of investigation is located along the northern part of Kerala coast extending between Kasargod and Manjeswar (figure 1). Earlier work in this region was confined to the extent of assessing the groundwater potential and locating suitable sites for sinking wells (Raghavarao 1975). Work on the chemistry of groundwater in relation to the aquifer characteristics of this region is lacking.

2. Hydrogeology

The topography of Kerala is such that the area can be divided into highland, midland and lowland regions. Precambrian crystalline rocks occupy the highlands whereas the midlands consists of Tertiary group of sediments with a thick laterite cover. Part of these members and the coastal alluvium, beach and dune sands cover the lowlands. A

Figure 1. Geological and well location map of the area.

generalized lithology of the area adopted from Paulose and Narayanaswamy (1968) is shown in table 1.

The laterite forms a distinct zone on top of the Tertiary sediments and is a potential aquifer in this region. Outcrops of sandstone and clays are encountered within the laterites at a number of places (along road cuts and quarries near Uppala and south of Kasargod) thus indicating an undulating topography of the Tertiary formations. Unconsolidated sands are sometimes seen lining the lower zone of the laterites in certain road cuts. The Tertiaries invariably contain siderite and pyrite. The thickness of the laterite formation varies from 3 to 15 meters. The open wells partially penetrate into the aquifer. The aquifer is recharged mainly by rain (annual rainfall is about 3000 mm) as the water levels show corresponding seasonal fluctuation. The water table levels fluctuate from 0.4 to 13.2 meters above the mean sea level during pre-monsoon and post-monsoon seasons and always lie above the mean sea level (table 2).

The area is drained by four rivers (figure 1) which develop into estuaries at their mouths. The chemical data on the river samples show that the seawater intrudes as far

Table 1. Lithology of the Tertiary sequence in Kerala.

Recent	Soil, alluvium, beach and dune sands lime shells, marine and esturine formations.
	 unconformity
Tertiaries	Laterites, variegated sandstones interbedded with plastic clays and variegated clays, carbonaceous clays with lignite seams, fossiliferous limestones.
	 unconformity
Archeans	Charnockites, khondalites, gneisses and migmatites.

Table 2. Water levels in the open wells (above m.s.l.).

Well No.	1	2	3
K1	0.8	1.5	0.9
K2	2.7	1.3	0.4
K3	1.3	2.2	1.3
K4	4.3	5.2	4.5
K6	1.1	6.3	1.7
K7	1.4	2.6	1.7
K9	1.2	2.1	1.3
K10	0.4	0.8	0.6
K11	2.2	4.4	2.8
K13	1.4	3.3	1.7
K14	2.2	4.0	3.3
K15	3.2	3.5	3.1
K17	1.6	2.5	2.4
K18	12.0	13.2	12.4
K19	7.1	8.5	7.6
K20	1.7	1.8	1.9

All values in meters. 1, 2 and 3: pre-monsoon, monsoon and post-monsoon data respectively.

as 15 km towards the land, thus indicating gentle bed slope of the river. The surface and groundwater chemistry, as will be shown later, indicate that the river system in this region is effluent and does not contribute much to the aquifer chemistry.

3. Hydrogeochemistry

Sixteen dug wells, shown in figure 1, were selected to monitor the water levels and water chemistry during 1982–83 hydrological year. The samples from these open wells were collected during pre-monsoon (February to March), monsoon (June to October) and post-monsoon (December to January) periods and analysed. The analyses are shown in table 3. The chemical analyses of groundwater occurring in a typical laterite terrain are also incorporated here for comparison and are shown in table 4. River water samples collected near the coast and at various points away from the coast were also analysed and the results are reported in table 5 along with the chemical analysis of the Arabian seawater collected near the coast.

Table 3. Chemical analyses of water samples from wells.

Well No.		Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	pH
K1	1	0.30	0.30	0.06	tr	0.12	0.17	0.36	6.1
	2	0.17	0.13	0.03	tr	0.10	0.10	0.15	7.7
	3	0.40	0.24	0.07	tr	0.27	0.17	0.31	6.1
K2	1	0.28	0.11	0.10	tr	0.07	0.02	0.41	5.5
	2	0.25	0.27	0.03	tr	0.19	0.01	0.35	7.9
	3	0.31	0.12	0.07	tr	0.21	0.02	0.30	6.1
K3	1	4.65	3.04	1.43	tr	0.62	1.43	7.09	6.5
	2	1.70	0.72	0.17	tr	0.52	1.00	1.01	8.0
	3	3.10	2.10	0.69	tr	0.46	0.67	4.67	nd
K4	1	7.81	3.81	1.76	tr	1.39	1.09	10.90	7.6
	2	2.65	1.16	0.08	tr	0.94	0.85	2.06	7.9
	3	1.60	4.20	0.22	tr	1.14	1.66	3.23	6.2
K6	1	0.18	0.50	0.03	tr	0.09	0.05	0.58	5.7
	2	0.30	0.30	0.02	tr	0.06	0.05	0.52	7.2
	3	0.48	0.37	0.03	tr	0.13	0.07	0.69	7.5
K7	1	0.95	0.16	0.03	tr	0.61	0.08	0.46	6.7
	2	0.21	0.16	0.04	tr	0.16	0.04	0.20	7.1
	3	0.53	0.14	0.07	tr	0.44	0.05	0.25	6.6
K9	1	0.75	0.45	0.06	tr	0.44	0.14	0.70	6.4
	2	0.68	0.26	0.04	tr	0.43	0.12	0.43	7.5
	3	0.75	0.26	0.08	tr	0.29	0.11	0.68	7.3
K10	1	7.60	3.14	0.39	tr	2.69	1.16	7.28	7.3
	2	1.61	0.57	0.14	tr	1.19	0.20	0.94	8.4
	3	4.00	1.81	0.35	0.02	2.62	1.36	2.18	7.2
K11	1	0.42	0.10	0.03	tr	0.20	0.02	0.34	6.0
	2	0.77	0.23	0.02	tr	0.28	0.50	0.25	7.3
	3	0.44	0.76	0.03	tr	0.23	0.69	0.31	5.5
K13	1	0.98	0.14	0.04	tr	0.74	0.03	0.39	6.5
	2	0.82	0.16	0.05	tr	0.52	0.04	0.50	7.8
	3	0.50	0.32	0.07	tr	0.23	0.03	0.59	6.1
K14	1	0.65	0.44	0.06	tr	0.20	0.22	0.72	5.5
	2	0.66	0.45	0.15	tr	0.35	0.21	0.71	7.4
	3	0.37	0.41	0.18	tr	0.25	0.33	0.60	5.3
K15	1	1.65	0.60	0.07	tr	0.27	0.83	1.20	6.2
	2	0.66	0.46	0.05	tr	0.35	0.60	0.22	7.5
	3	1.05	0.96	0.05	tr	0.34	1.09	0.63	5.3
K17	1	5.20	2.92	0.27	tr	2.87	0.83	4.69	6.9
	2	2.00	0.99	0.13	tr	1.01	1.00	1.11	7.9
	3	2.34	1.46	0.14	tr	1.13	1.60	1.22	6.1
K19	1	1.11	0.71	0.05	tr	1.29	0.25	0.32	7.6
	2	1.81	1.57	0.47	tr	1.46	0.72	1.69	8.1
	3	1.76	1.70	0.67	tr	1.29	0.44	2.40	6.1
K20	1	0.90	0.48	0.16	tr	0.29	0.52	0.73	6.2
	2	3.28	1.60	0.74	tr	1.70	1.20	2.72	8.0
	3	1.25	1.09	0.05	tr	0.21	1.58	0.60	5.3

All values in epn. tr: in traces.

Table 4. Chemical analyses of water in laterite aquifer.

	1 (72)	2 (192)	3 (888)	4 (1400)	5	6
pH	6.8	6.5	6.5	6.5	6.6	6.1–7.7
Ca	0.099	0.149	0.299	0.249	0.039	0.099–0.690
Mg	0.016	0.023	0.057	0.070	0.029	0.016–0.510
Na	0.075	0.044	0.108	0.139	0.143	0.030–0.160
K	0.015	0.023	0.028	0.041	0.005	0.001–0.032
HCO_3	0.065	0.082	0.192	0.321	0.065	0.033–0.820
SO_4	0.010	0.015	0.017	0.010	0.010	0.062–0.100
Cl	0.130	0.137	0.282	0.169	0.141	0.056–0.423

1–4: experimental laterite-water interaction (Chandrasekharam 1984). Numbers in parenthesis indicate contact hours between rain water and laterite; 5: chemical analysis of rain year 1982; 6: groundwater analysis in a typical laterite aquifer (total number of analyses 159; data from Chandrasekharam and Ushakumari 1983); all values in epm.

Table 5. Chemical analyses of river and seawater.

	7	8	9	10	11	12
pH	7.6	7.2	7.1	7.0	7.0	6.5
Ca	13.97	11.98	9.98	10.48	2.2	19.46
Mg	100.64	79.98	64.22	43.17	0.71	99.92
Na	316.70	273.91	200.00	106.52	0.22	1130.00
K	53.07	22.81	12.56	2.30	0.01	128.00
HCO_3	1.72	1.31	1.15	1.06	0.74	1.83
SO_4	41.37	34.73	29.12	20.92	0.98	75.47
Cl	441.17	352.62	256.50	140.42	1.41	1300.00

7: sample near the river mouth; 11: sample about 15 km away from the mouth towards the upstreamside; 8–10: samples at points between locations 7 and 11; 12: Arabian seawater. values in epm. River samples were collected from Chandragiri river.

Laterite-water interaction experiments were also carried out to have a better control over the chemical characteristics of groundwater occurring in this aquifer. Laterites derived from the Precambrian gneisses and chronockites were made to react with rain water. The experiment was carried out in 100×10 cm glass columns and the system was open to the atmosphere (uncontrolled Pco_2 condition) at room temperature (30°C). Water samples from the columns were collected at different time intervals and analysed. The results are shown in table 4.

The pH and conductivity of the samples were measured in the laboratory immediately after collection of the samples. The methods recommended by APHA (1975) were adopted to determine the dissolved constituents in the samples.

The chemical analyses of all the samples analysed were plotted on the orthodox Piper diagram (Piper 1944) shown in figure 2 to examine their chemical behaviour. The groundwater occurring in laterites, as evident from the experimental data and also from the groundwater data in a typical laterite aquifer, should possess HCO_3 ions in excess of SO_4 and Cl ions and plots should fall in the bicarbonate facies. But the

Figure 2. Piper diagram showing the various geochemical facies of groundwater. A, B and C: Fields of groundwater from the study area during pre-monsoon, monsoon and post-monsoon seasons respectively. Striped field in A shows the field of groundwater in a typical laterite aquifer. Striped field shows the field of river-seawater mixture. For numbers refer tables 4 and 5. a: Ca + Mg bicarbonate facies; b: Na + K bicarbonate facies; c: Na + K chloride and sulphate facies; d: Ca + Mg chloride and sulphate facies.

water samples from the study area record larger incidence of SO_4 and Cl ions relative to HCO_3 and fall in the $\text{SO}_4 + \text{Cl}$ facies. Although these samples show temporal variation, this variation is limited to the $\text{SO}_4 + \text{Cl}$ facies only (figure 2). The post-monsoon season samples possess higher SO_4 content and SO_4/Cl ratio relative to the other two seasons. It is interesting to note the lack of any relationship between the alkali ions and Cl ions (table 3). Even the sample with the highest Cl concentration of 386 ppm (K4, table 3) registered only 40 ppm of total alkalis. The water samples record higher pH values (above 7) during monsoon while during the remaining seasons the pH values fall below 7 (table 3). A negative correlation is noticed between the pH and SO_4 during post-monsoon season.

4. Discussion

All the wells in the area partially penetrate into the aquifer (table 1) and the water levels always lie above the mean sea level. The higher incidence of SO_4 and Cl ions relative to HCO_3 ions is generally attributed to the mixing of seawater, for, intrusion

Figure 3. SO_4/Cl vs SO_4 diagram showing the fields of groundwater from the study area, groundwater occurring in a typical laterite aquifer, river-seawater mixtures. For numbers refer tables 4 and 5. P: pre-monsoon; M: monsoon; and Pt: post-monsoon.

Figure 4. Mg/Ca vs Cl diagram. Symbols same as in figure 3.

of seawater into the coastal aquifers is common. It has been demonstrated earlier, using a sea-aquifer water mixing model, that intrusion of seawater along this coast takes place only when the gradient is reversed due to excess withdrawal of water from these wells (Chandrasekharam 1985). However, in the present case there is no indication of negative gradient prevailing in this area (see table 1). As evident from the chemical data (table 3) the Cl, Na and K ions do not show any systematic relationship which is otherwise expected if seawater mixing is taking place. This puts a constraint on the seawater mixing hypothesis. Let us examine this phenomena using SO_4/Cl vs SO_4 and Mg/Ca vs Cl diagrams as shown in figures 3 and 4. As for example, the river water samples mixed with seawater in different proportions lie on the river-seawater tie line thus showing clear indication of mixing (figures 3 and 4). By applying similar analogy, if the higher concentration of SO_4 and Cl in the water samples is assumed to be due to seawater mixing, then the concentrations of Ca, Mg, SO_4 and Cl ions in the mixtures should lie within the boundaries of the tie line between the Arabian seawater and laterite aquifer water field in figures 3 and 4. Further, if it is argued that the Ca and Mg concentrations of the mixtures need not lie between the two end members due to their sorption by clays then at least the SO_4 and Cl ions, which do not interfere with the clay-water system, should lie on this line.

Further, the water levels always lie above the mean sea level and fluctuation in the levels during post-monsoon and pre-monsoon seasons is marginal varying from 0.1 to

0.8 meters except in two wells where the fluctuation is considerable, varying from 1.1 (K14) to 2.3 (K2) meters (table 2). If the Ghyben-Herzberg seawater intrusion mechanism is envisaged, then the SO_4 and Cl concentrations in the wells K2 and K14 should show increase relative to the other wells. On the other hand wells K3, K4 and K10 which show negligible water level fluctuation during the above seasons, record the highest SO_4 and Cl concentrations (table 3). Thus the water chemistry and water level data put severe constraint in advocating seawater mixing process in this region. The alternate source which could supply SO_4 and Cl ions to the aqueous system is the Tertiary sediments consisting of various members listed in table 1. These sediments were deposited under marine environment along the continental marginal basins of the west coast of India (Raha *et al* 1983). It is only natural to expect them to retain old sea salts at the time of deposition and release them subsequently during their interaction with the water recharging the aquifer. Cases of groundwater contamination with connate water of marine origin were reported from Gujarat coast (Desai *et al* 1979). The absence of systematic relationship between Na + K and Cl ions could be explained by the presence of clays which form excellent exchangeable sites for these two ions. Besides these old sea salts, iron sulphides which are present in the sediments also contribute SO_4 to groundwater. This is especially so during the post-monsoon season where the SO_4 increase is considerable (figure 2). An inverse relationship between SO_4 and pH in the water samples during this season (see table 2) gives evidence of breakdown of sulphides to SO_4 thus releasing H ions into the aqueous system.

5. Conclusions

The groundwater along the Kasargod-Manjeswar coast shows large incidence of SO_4 and Cl relative to HCO_3 ions and plot in the $\text{SO}_4 + \text{Cl}$ facies instead of HCO_3 facies to which the water in laterite aquifer generally belongs to. The absence of any systematic variation of these ions together with the data obtained on the river water and Arabian seawater and the lack of sympathetic relationship between the Cl and Na + K ions rule out the possibility of seawater mixing with the aquifer in this region. The water level data also corroborate with the above view. The Tertiary sediments which retain old sea salts are responsible for enhancing SO_4 and Cl ions concentration in the groundwater. These salts were caught during the time of deposition and consolidation of the sediments under marine environment. The available Na and K ions in these old sea salts were absorbed by the clays on their exchangeable sites.

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