



Chemical Evolution of Groundwater in the Coral Islands of Lakshadweep Archipelago, India with Special Reference to Kavaratti Island

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ABSTRACT

This paper discusses the unique hydrochemical environment of Lakshadweep Archipelago, a cluster of coral islands, where groundwater exists in the form of a thin freshwater lens over the saltwater, having restricted lateral movements. The influence exerted by the shape of these tiny islands on the stability of the water in the lenses and the tendency of this water to mix with seawater are elucidated. The factors which influence the chemical evolution of groundwater in these islands, such as the geochemistry of the coral aquifer, mixing of sea water, dissolution of CaCO_3 , marine aerosols and cation-exchange processes are discussed. Mixing of seawater was found to be the predominant process controlling the configuration of freshwater lenses in these islands, as reflected in the ion-ratio studies and the major ionic species observed. The hydrochemical facies, identified with the freshwater lens, represents various phases of mixing. Metabolism of the biological organisms and diagenesis of the lime shells in the corals are responsible for the relatively higher concentration of trace metals, such as strontium and iodide in this aquifer system.

INTRODUCTION

Lakshadweep Archipelago consists of 36 small oceanic coral islands, of which 10 are inhabited. These coral islands are located between North Latitudes $8^{\circ}00'$ and $12^{\circ}30'$ and East Longitudes $71^{\circ}00'$ and $74^{\circ}00'$ in the Arabian Sea on the west coast of India (Fig. 1). The total area of these islands is 32 sq. km (Mannadiar 1977).

The small oceanic islands differ from the mainland and the major islands in their aquifer geometry and hydrochemistry. In these small oceanic islands, fresh groundwater occurs as a lens floating over the saline water, and the freshwater lens is in hydraulic continuity with seawater. The variation in quality is more pronounced in the margins of the freshwater lens than at its centre (Najeeb & Vinayachandran 2006). The coral islands are composed of calcareous sand and the materials derived from coral atoll, which are of very high purity and chemical grade, with 87 percent CaCO_3 (Najeeb & Vinayachandran 2011). In this archipelago, the Deccan Traps and associated volcanics form the basement on which thick sediments are deposited from Palaeocene onwards (Siddique et al. 1976). The sand comprises of beach facies, strandline facies, dune facies and their anthropogenically modified variants. The sediments of the lagoon and the terrestrial part of the islands consist chiefly of various types of coral materials formed by fragmentation of reefs due to wave action. The beach rocks of the islands consist of moderately well-cemented calcarenites, composed of reef detritus, usually dominated by skeletal fragments of

corals, coralline algae, other algae, molluscs, foraminifera, and echinoderms in order of abundance (Nair 1982).

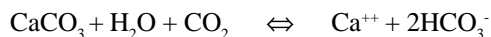
The hydrochemistry of these islands is sensitive to groundwater-draft and recharge, and evolves mainly through mixing of waters, cation-exchange processes, marine aerosols and CaCO_3 dissolution. The aerosols in the atmosphere influence the rainwater quality, and the concentration of chloride in rainwater is less in the interior of the island than at the coast, as the thick vegetation in the interior obstructs the aerosols. This was revealed by the higher electrical conductivity (EC) of $320 \mu\text{S}$ recorded during the rainfall at Dak Bungalow (Fig. 2), which is within 20 m from the coast, as against only $210 \mu\text{S}$, about 50 m from the coast, in Kavaratti Island. The hydrogeology of Kavaratti island is depicted in Fig. 2. Groundwater samples were analysed from 98 locations in various islands, of which 35 samples from Kavaratti Island were studied in detail.

CHEMISTRY OF GROUNDWATER IN THE ISLANDS

The major ions in this coral aquifer system reflect the general hydrochemical scenario and are tabulated in Table 1.

The concentration of major ions in the freshwater lens is within the permissible limits, and fluoride varies from 0.12 to 2.1 ppm. The changes in the quality of groundwater are lateral, vertical and temporal. The freshwater lens is generally alkaline, with pH ranging from 7.16 to 8.61. The dissolution of CaCO_3 during rainwater infiltration leads to high pH of groundwater. However, the samples from the pumping wells

immediately after pumping are slightly acidic. This is because of the precipitation of CaCO_3 from water due to the instability of equilibrium developed between calcium and bicarbonate ions. CaCO_3 precipitation is often seen at the bottom of such pumping wells. The decrease of pressure that accompanies pumping from a certain depth below water level is likely to cause a decrease of dissolved CO_2 , and to render the water more saturated with calcite than it originally was (Mandal & Shiftan 1981). The overall reaction describing CaCO_3 dissolution and precipitation is given below:



ASPECT RATIO OF THE ISLANDS

It is observed that the variation in the quality of groundwater is pronounced in the elongated and narrow islands like Agatti and Kadamat, unlike in the oval-shaped or circular islands like Kavaratti and Androth. The aspect ratio has a bearing on the stability of freshwater lens. The aspect ratio is obtained by dividing the area of the island by the ratio between

its length and breadth (Table 2). Under identical hydrogeological conditions, the freshwater lens is stable in the islands having an aspect ratio of more than 0.5 (Najeeb 2004).

CHEMICAL EVOLUTION OF GROUNDWATER IN KAVARATTI ISLAND

A detailed analysis of the hydrochemical data from Kavaratti island (Fig. 2) is conducted in order to elucidate the hydrochemical processes. Water samples were analysed for major ions and important minor ions such as fluoride, iodide, boron and strontium (Table 3). The chloride content shows a wide variation from 46 to 2591 ppm, while the variation in alkalinity is far less pronounced. The relative concentration of major ions as percent equivalents of anions and cations is plotted in the trilinear diagram (Fig. 3) to identify the hydrochemical facies, for comparing the origins and distribution of groundwater masses (Piper 1944, Hem 1970, Lloyd & Heathcote 1985). The samples falling in Ca-Mg-

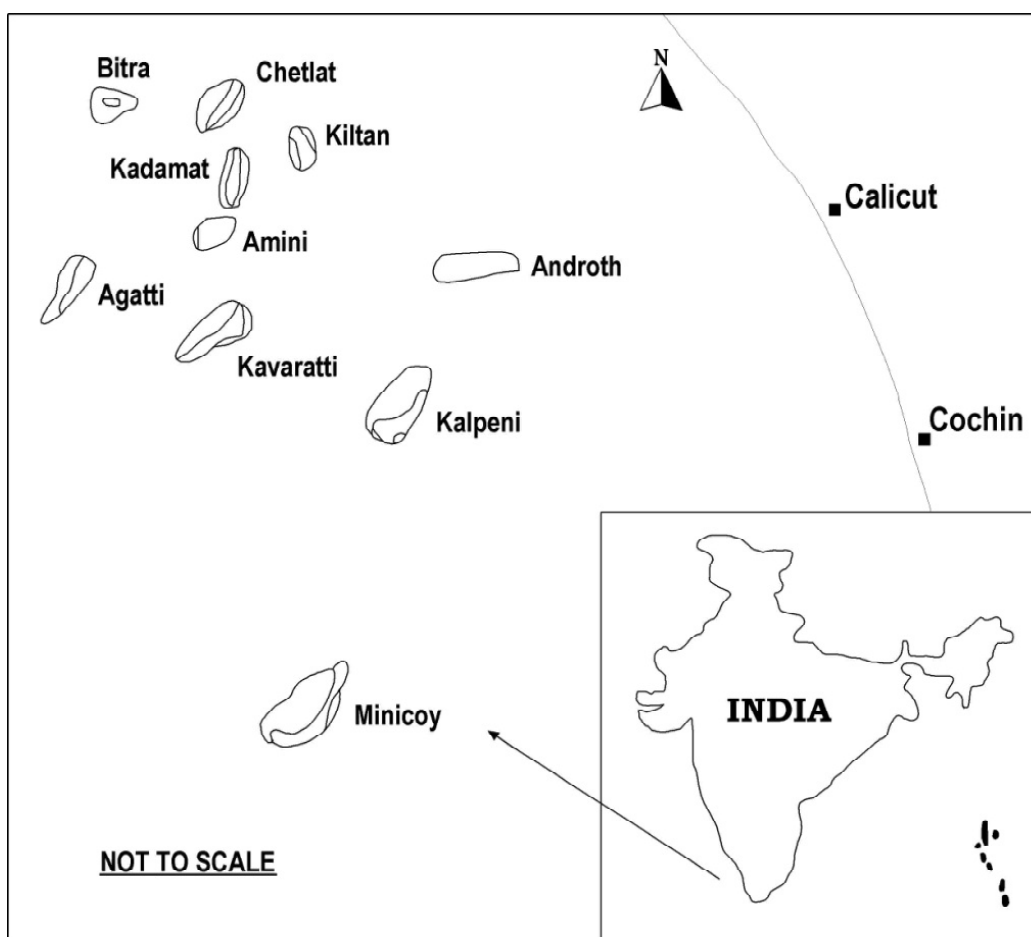


Fig. 1: Location map of the study area.

HCO₃ field are those obtained from the northern part of the island representing the stable freshwater lens.

The samples from Na-Cl field and the central part of the diamond field are characterized by mixing of waters, and were obtained from the southern tapering part and from the eastern periphery of the island.

Bicarbonate is derived as a result of the dissolution of the coral formation by the percolating rainwater containing CO₂. The solution activity of the percolating rain on the geological formation being uniform throughout the island, the bicarbonate content does not show any significant variation. On the other hand, the chloride ion, being a component of seawater, shows a wide variation, depending on the rate of groundwater draft, the transmissivity of the aquifer material and the proximity of the location to saline water body (Varma

1997). The mean Na/Cl ratio in the groundwater in Kavaratti Island is 0.87, which is very close to that of seawater (0.86), indicating that sodium as well as chloride is of marine origin (Stumm & Morgan 1981). Further, the perfect correlation observed between Na and Cl (Fig. 4) supports this conclusion.

However, the perfect linear relation observed at low concentrations can be attributed to the activity of marine aerosol. The sodium chloride accumulated in the topsoil by marine aerosols gets washed down along with the infiltrating rainwater.

The correlation-coefficient matrix for chemical parameters of 35 samples from Kavaratti island indicates the existence of several groups of significantly related constituents at 99.5% confidence level (Table 4). TDS, Cl⁻, SO₄⁻²,

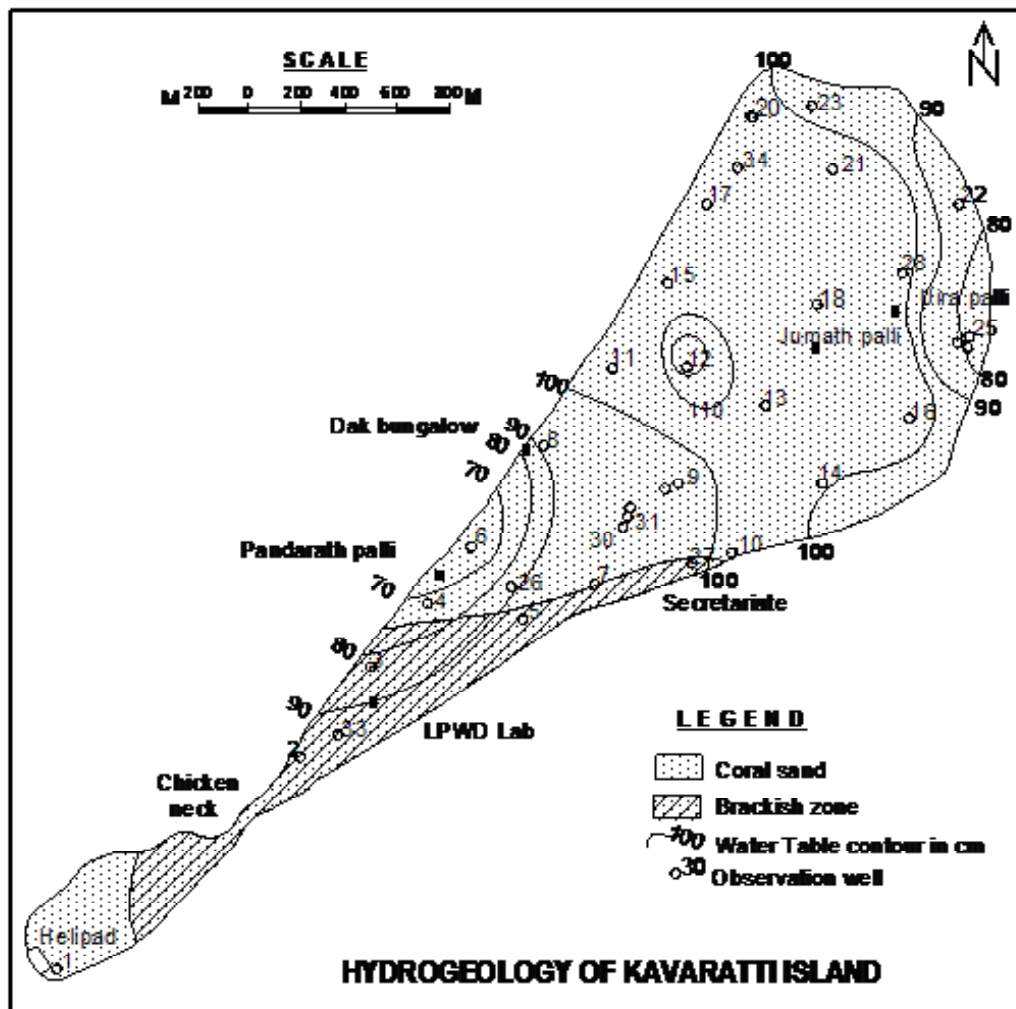


Fig. 2: Hydrogeology of the island and location of sampling points

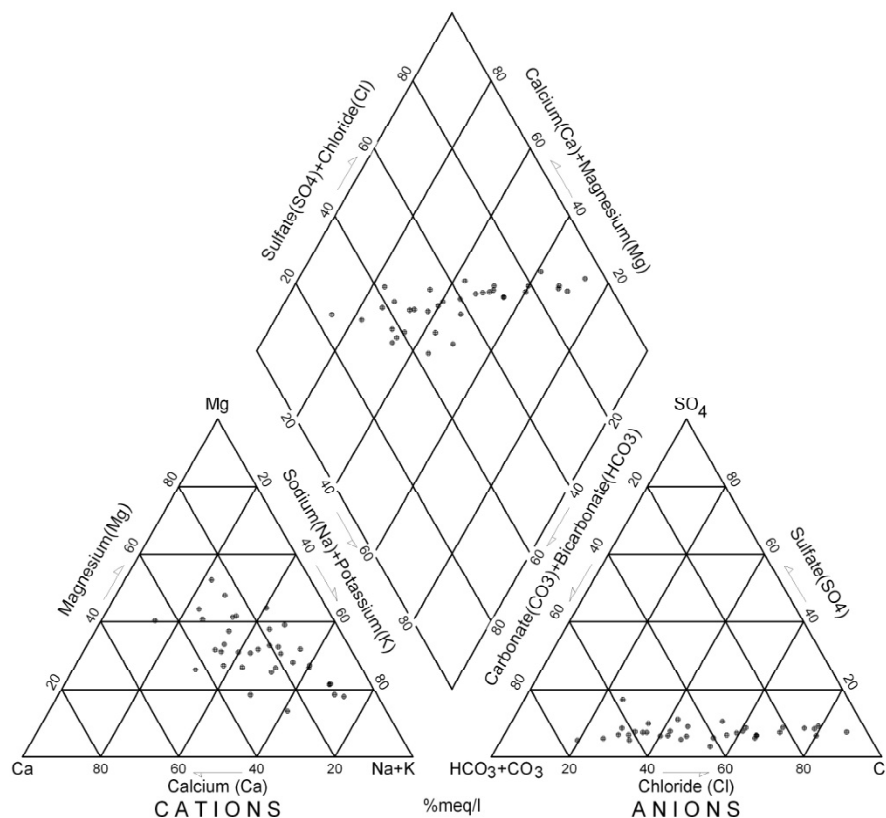


Fig. 3: Hill-Piper diagram showing hydrochemical facies of groundwater in Kavaratti island.

Table 1: Hydrochemical scenario in the Lakshadweep Islands.

Island	Area sq.km	No. of Samples	pH	EC in $\mu\text{S/cm}$	TH	Ca	Mg	Concentration in ppm					
								Na	K	HCO ₃	SO ₄	Cl	F
Kavaratti	3.63	35	7.16-8.22	601-8300	190-800	28-172	28-183	20-1340	0.4-70	165-854	16-335	46-2591	0.2-2.1
Agatti	2.7	7	6.91-7.21	810-4300	305-600	70-134	27-109	54-552	4.5-64	415-836	25-130	103-1108	0.5-1.16
Amini	2.59	13	7.13-7.43	880-3700	330-790	38-112	39-111	52-555	4.8-28	317-702	24-155	99-923	0.12-1.4
Chetlat	1.04	4	7.93-8.51	690-2700	230-580	34-92	35-95	nd	nd	110-451	nd	110-682	nd
Kadamat	3.13	6	6.86-7.58	500-2800	215-680	46-150	28-74	21-288	0.4-10	249-549	nd	36-650	nd
Kiltan	1.63	5	7.76-8.61	380-4500	135-700	22-112	19-102	nd	nd	116-329	nd	43-1328	nd
Kalpeni	2.28	5	7.21-7.62	730-2100	335-655	96-144	23-72	11-154	1.5-5.8	372-531	nd	57-483	nd
Androth	4.80	12	7.01-7.64	520-1740	280-585	78-116	11-81	5.2-150	tr-17	335-640	9-55	11-341	0.16-1.52
Minicoy	4.40	11	7.12-7.97	340-2500	120-690	32-198	9.7-66	19-204	1.7-122	152-604	15-278	25-433	0.32-1.2

nd - no data available, tr - traces

Table 2: Shape and aspect ratio of the main islands of the Lakshadweep.

Location	Kavaratti	Agatti	Amini	Chetlat	Kadamat	Kiltan	Kalpeni	Androth	Minicoy
Area (sq.km)	3.63	2.70	2.59	1.04	3.13	1.63	2.28	4.80	4.40
Maximum length (km)	5.5	7.6	2.89	2.5	8.0	3.36	5.0	4.6	10.66
Maximum width (km)	1.4	0.9	1.25	0.65	0.55	0.60	1.25	1.5	0.94
Aspect ratio = A/(L/B)	0.9	0.3	1.1	0.3	0.2	0.3	0.6	1.6	0.4
Shape	Bottle gourd	Base ball stick	Oblong	Sole	Elongated	Elongated	Club	Elliptical to sole	Crescent

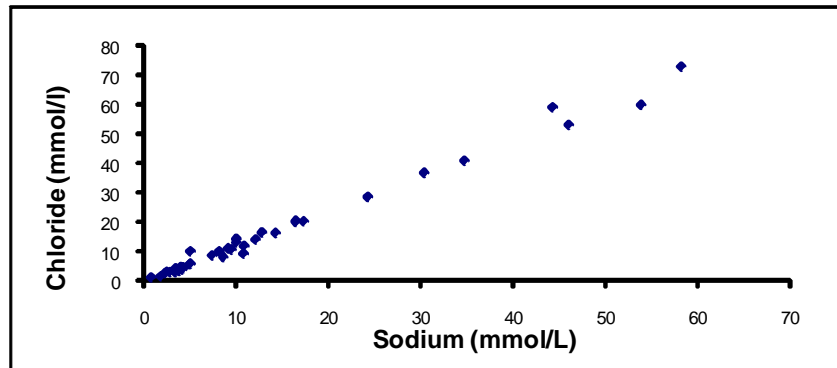


Fig. 4: Correlation between sodium and chloride.

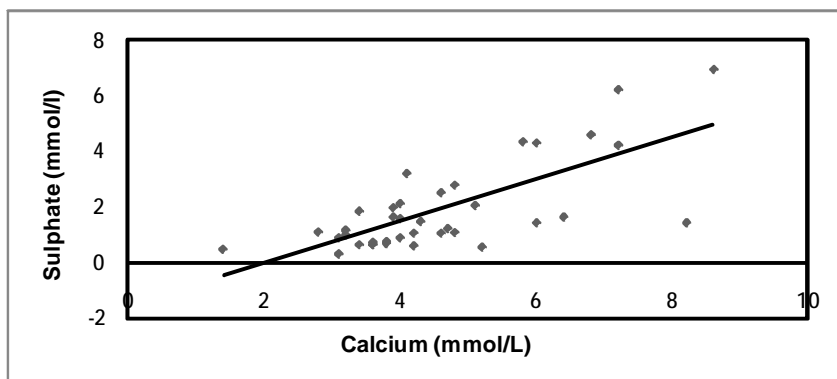


Fig. 5: Correlation between calcium and sulphate.

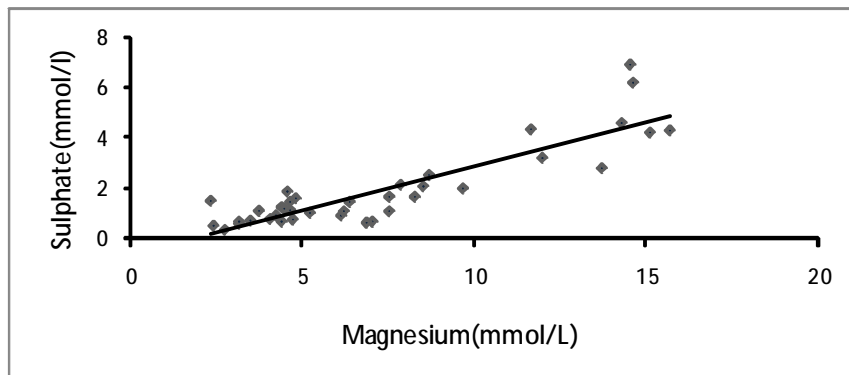
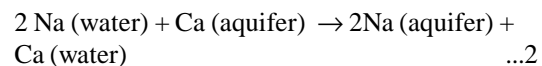
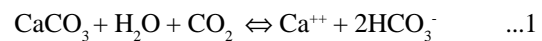


Fig. 6: Correlation between magnesium and sulphate.

Na⁺, K⁺ and Mg⁺² are highly correlated among themselves. HCO₃⁻ has significant correlation with F⁻, Mg⁺² and TDS.

Aquifer mineralogy and the presence of clay minerals play a significant role in the ion-exchange process. However, coral aquifers are devoid of clay minerals, and they mainly consist of coral sands and shells (CaCO₃). Cation exchange of sodium of seawater for calcium of aquifer material and dissolution of CaCO₃ are the major chemical activities in this aquifer system, apart from the daily and seasonal mixing of seawater.



Normally, groundwater exchanges calcium for sodium in a groundwater-flow regime. But, in the present situation, there is limited scope for exchange of sodium ion in the aquifer material for calcium ion in the water due to lack of efficient adsorbing material like clay in the aquifer system. The high sodium concentration observed is mainly due to

Table 3. Chemical quality of groundwater samples from Kavaratti island.

Well No.	pH	EC in $\mu\text{S}/\text{cm}$ at 25°C	TDS	Ca	Mg	Na	K	Concentration in ppm								
								HCO ₃	SO ₄	Cl	F	I ($\times 10^{-3}$)	B	NO ₃	PO ₄	Sr
1	7.65	1960	330	86	28	232	9.8	165	72	469	0.2	55	nd	28	0.09	1.7
2	7.69	8260	1090	144	177	1340	65	268	300	2591	0.9	21	0.63	29	nd	nd
3	7.76	5460	870	116	141	800	70	415	210	1455	1.2	12	0.27	50	nd	3.3
4	7.78	1970	440	80	58	212	4.9	342	77	398	0.9	10	0.12	32	0.59	nd
5	7.52	3110	675	78	117	380	4.5	549	96	717	1.4	18	0.21	8	0.17	4.4
6	7.66	3220	680	102	103	380	8.9	561	100	731	1.3	9	0.33	10	0.03	nd
7	7.52	3040	800	82	145	330	7.7	659	155	582	1.9	31	0.24	15	0.21	nd
8	7.46	2580	695	128	91	232	14	561	80	511	1.5	12	0.46	15	0.04	5.7
9	7.58	2180	605	78	100	200	37	781	80	291	1.9	67	0.37	9	0.14	nd
10	7.65	1250	460	62	74	81	1.5	439	44	156	1.4	22	0.26	5.7	0.11	2.7
11	7.74	1490	455	94	53	100	23	317	60	167	0.9	9.5	nd	212	0.05	nd
12	7.75	1430	425	96	45	118	2.5	439	53	213	1.0	17	nd	8	0.13	nd
13	7.74	1150	415	104	38	86	2.7	439	28	135	0.8	12	nd	4.5	0.17	2.8
14	7.54	2130	585	84	91	250	17	610	52	334	1.6	76	nd	tr	0.11	nd
15	7.87	1040	400	72	53	59	7.5	378	32	114	1.2	14	nd	14	0.18	nd
16	7.92	650	290	62	33	20	2.3	305	16	46	0.6	3.5	0.26	13	0.11	nd
17	7.66	1240	410	80	51	97	7.5	439	44	142	1.1	11	nd	19	0.09	2.6
18	8.22	601	190	28	29	44	0.9	220	24	60	0.7	13	nd	tr	0.05	nd
19	7.81	1020	395	68	55	55	0.4	390	90	99	1.1	11	nd	4.3	0.27	2.9
20	7.8	1250	415	72	57	94	8.5	390	36	170	0.9	45	nd	27	0.05	nd
21	7.91	1200	335	72	38	100	28	329	32	156	1.5	16	nd	60	0.02	nd
22	7.4	2660	615	120	77	296	2	464	70	589	1.3	22	nd	tr	0.05	nd
23	7.61	2010	540	92	75	190	13	464	52	362	1.3	36	nd	20	0.16	2.7
24	7.55	1240	390	76	49	116	4.9	354	37	206	1.6	nd	nd	2.5	nd	2.6
25	7.84	1110	420	64	63	90	9.1	342	49	128	1.7	nd	nd	30	nd	2.7
26	7.47	1530	370	56	56	172	6.8	281	54	312	1.9	34	nd	10	nd	nd
27	7.31	2910	590	80	95	400	16	397	103	724	1.7	19	0.06	5.3	0.01	nd
28	7.36	1080	360	76	42	80	6.5	415	34	110	0.7	8	0.04	28	0.03	nd
29	7.38	1120	520	68	85	67	2.1	500	32	110	2.1	nd	nd	tr	0.1	4.4
30	7.16	1310	550	84	83	220	4.1	512	30	383	2.0	nd	nd	11	nd	nd
31	7.3	3160	920	96	166	280	12	854	135	504	1.2	nd	nd	3	nd	nd
32	6.98	6740	1110	144	183	1060	46	549	204	1889	1.12	39	0.44	32	0.15	5.7
33	7.2	8300	1150	172	176	1240	70	537	335	2130	0.9	nd	nd	75	nd	nd
34	7.18	2890	640	164	56	252	56	415	70	426	0.5	nd	nd	420	0.11	nd
35	7.29	5560	1050	136	173	700	40	671	222	1310	1.6	44	0.42	12	0.23	nd

nd- not determined, tr- present in traces

mixing of seawater. The mixing of seawater and the cation-exchange process in such mixing zones, where the seawater exchanges sodium ion for calcium in the aquifer, evolves the Ca-Mg-HCO₃ type water of the freshwater lens to Na-Cl type water. These different stages of ion exchange and mixing lead to the development of different hydrochemical facies, as revealed in the Hill-Piper diagram (Fig. 3).

The advancing saltwater front generally carries a higher level of calcium in proportion to sodium, than is characteristic of seawater. The major cation-exchange process that takes place in these islands is due to the advancement of seawater into the freshwater domain. The cation-exchange process is also evident from the high calcium-sodium mole ratios compared to that in seawater (Mercado Abraham 1985).

The magnesium concentration in 19 samples is found to

be higher than or equal to that of calcium. A lower concentration of magnesium compared to calcium is normally observed in groundwater environment. Magnesium-dominant groundwater is found in dolomitic terrain. In coral islands and limestone terrain, magnesium occurs in significant amounts, but it is seldom found to have dominance over calcium. Dissolution of limestone and the consequent release of the adsorbed magnesium from it is the source of magnesium in groundwater. This being the only source of magnesium in the island, a reasonable correlation can be expected between calcium and magnesium ions in the groundwater. However, the dominance of Mg over Ca in the water may be due to the involvement of other factors influencing the concentration of these ions, than the dissolution process. Once magnesium is released to groundwater as a result of dissolution, the process is not

Table 4: Correlation coefficient matrix of water samples from Kavaratti Island.

	EC	TDS	Ca	Mg	Na	K	HCO ₃	SO ₄	Cl	F
EC	1									
TDS	0.929*	1								
Ca	0.796*	0.79	1							
Mg	0.874*	0.968*	0.612*	1						
Na	0.988*	0.885*	0.744*	0.838*	1					
K	0.825*	0.721*	0.751*	0.624*	0.809*	1				
HCO ₃	0.26	0.559*	0.286	0.607*	0.17	0.124	1			
SO ₄	0.968*	0.903*	0.717*	0.872*	0.949*	0.786*	0.268	1		
Cl	0.985*	0.879*	0.742*	0.832*	0.997*	0.791*	0.146	0.944*	1	
F	-0.064	0.139	-0.214	0.266	-0.065	-0.14	0.462*	-0.048	-0.074	1

*Statistically significant correlation between variables at 99.5% confidence level

easily reversible. Hence, the magnesium concentrations may increase even under a situation where calcium precipitates as a result of oversaturation. This, in conjunction with the mixing of seawater, results in a high Mg:Ca ratio in some of the areas. The spatially distributed sample locations with a higher level of magnesium than calcium are situated either in the southern half of the island or in the coastal part, where the freshwater lens has a tendency to mix with seawater (Fig. 2). Mg:Ca ratio is high in seawater. This is because of the higher consumption of Ca by marine organisms. The mixing zones in the island have a distinct, high Mg:Ca ratio.

The presence of sulphur in calcium sulphate as gypsum (CaSO₄·2H₂O) or as unhydrated which contains no water molecule, is common in a limestone terrain. These minerals are seldom found in any significant level in coral islands, even though sulphur is a major constituent in the groundwater. The aquifer material in Kavaratti island is composed of highly pure calcareous sand, having 87% CaCO₃. From the Ca:SO₄ ratio (Fig. 5) and Mg:SO₄ ratio (Fig. 6), it can be observed that there is an increase in SO₄, corresponding to the increase in Ca and Mg. This is because of the solubility characteristic of gypsum.

With an increase in the other solutes, the solubility of gypsum increases due to greater ionic strength and smaller activity coefficients. The plotting spread on either side of the main trend indicates the effect of other influencing factors such as mixing of waters, cation exchange, etc.

DISTRIBUTION OF TRACE ELEMENTS

The important minor components of seawater viz., fluoride, iodide, boron and strontium were analysed from the groundwater samples of Kavaratti island. Fluoride is present in low concentrations (normally less than 1.5mg/L), as it forms strong solute complexes with many cations. The spatial distribution of fluoride in the island varies in the range of 0.2 to 2.1 mg/L (Table 3). Calcium fluoride (CaF) in the skeletal remains of marine organisms is the major source of

fluoride in the coral islands.

The strontium content of the groundwater is in the range of 1.7 to 5.7 mg/L (Table 3), which is quite abnormal. Similarly, the Sr/Cl ratio in the groundwater is in the range of 0.002 to 0.06, which is 60 to 160 times greater than that in seawater. The higher content of strontium is attributed to biological origin from weathering and decay of corals (Najeeb 2004). The calcitic shells of microorganisms of recent age are dominated by the aragonite phase, whereas, those of the early tertiary and older ages are dominated by the calcite phase, as revealed from the X-ray-diffraction studies of the sedimentary formations of coastal Kerala (Jacks 1987). The Aragonite has higher strontium content than the calcite. The iodine content of the groundwater is in the range of 3.5 to 76 µg/L. The I/Cl ratio is in the range of 8×10^{-6} to 2.6×10^{-4} . Correlation between magnesium and sulphate is about 3 to 90 times higher than that of seawater (Fig. 6). The marine organisms derive iodine from seawater. These organisms, on decay, release the iodine into the groundwater, thereby increasing the concentration of iodine in it (Kcauskoof 1967). The boron content in the groundwater varies from traces to 0.6ppm. The boron concentration in the groundwater is not conspicuous.

CONCLUSIONS

The freshwater lens in the Lakshadweep islands is fragile and the shape of the islands plays a significant role in its occurrence and stability. When the hydrogeological conditions are identical, the freshwater lens in those islands with aspect ratio of less than 0.5 is more prone to mixing with seawater.

The chemical evolution of groundwater in the coral islands of Lakshadweep is due to the combined effect of various processes such as mixing of waters, contributions by marine aerosols, cation exchange, and dissolution of CaCO₃ etc. in varying proportions. These processes discussed above govern the relative concentrations of major ions in these

aquifers. The correlation matrix (Table 4) for the major ions shows a significant correlation among the ions Ca^{++} , Mg^+ , Na^+ , K^+ and SO_4^- , and HCO_3^- has a better correlation with Mg^{++} and F^- .

The different chemical facies identified in the freshwater lens are related to various phases of mixing of seawater in lateral and vertical directions. The dominant factor modifying the chemistry of the freshwater lens appears to be the mixing of seawater, with the other factors such as cation exchange, dissolution of CaCO_3 and marine aerosols exerting their influence to a lesser degree.

The relatively high concentrations of trace elements viz., strontium and iodine are unlikely to have been caused by seawater mixing. Strontium is released into the groundwater as a result of the diagenesis of lime shells from aragonite structure to stable calcite structure, while iodide is released during the decay of marine organisms.

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