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THE CHEMICAL COMPOSITION OF SOME WATERS FROM DUNE SLACKS IN RAMESWARAM ISLAND, MADRAS STATE

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ABSTRACT

Analyses of pH, total dissolved solids, CO_3, HCO_3, Cl, SO_4, Ca, Mg, Na and K are presented for water samples from dune slacks in Rameswaram Island. Comparison of these analyses has been attempted with well waters from the area, sea water and world average fresh water. It is inferred that these slacks are under the influence of sea water but ion-exchange processes similar to those in arid alkali soils appear to be responsible for Ca/HCO_3 ratios of less than unity and Na/Cl and Mg/Cl ratios greater than those in sea water.

Exceptionally high Na_2CO_3 and $NaHCO_3$ contents in one of the slack waters is explained on the basis of sulphate reduction due to favourable conditions developed locally there.

INTRODUCTION

Although much is known about the vegetation of coastal sand dunes and slacks in Britain and some other countries, very little work has been carried out on the Indian sand dune flora and habitat. So far as the chemistry of environment of sand dunes and slacks is concerned, some studies have been carried out by Gorham (1958, 1961). Recently the vegetation of Rameswaram Island in th Madras State of India, which presents typical coastal sand dune and slack habitat, and a brief account of which in respect of the vegetation of slack habitat especially is reproduced below, has been worked out by Rao *et al.* (1963) on pioneering basis and the present paper a supplement to these studies presents a short account of the chemistry of the environment of sand dune slacks in the aforementioned island, which is separated from the mainland of Ramnad District only by a narrow passage known as Pamban Channel.

The dune slacks in Rameswaram Island, situated in the Gulf of Manaar, are periodically flooded either by rain water in the wet season or by sea water during rise of tide. In addition to the flooding by rain or sea water it will seem that there is an upward diffusion of sea water in these slacks by capillary action. At the time of collecting water samples from these slacks in the month of September although there was no surface water present in them and they looked dry apparently, the soil was very moist just at 1-2 cm depth and water was met at depths between 30-52 cm from surface level on digging. The composition of different ions in water samples from these slacks might have been influenced, therefore, by (i) rain water, (ii) sea water and (iii) minerals leached down from the sand dune soils, to different degrees depending on the location and position etc. of the individual slacks. Consequently the body of ground water in the surface layers of these slacks will be fresh to the extent that the addition of rain water overbalances the inward diffusion of sea water and the extent to which minerals from the sand dune soils have been leached down.

Ipomoea pes-caprae is one of the principal components of dune slacks with gregarious growth of *Nostoc* sp. at the periphery in the wet season, when surface water is present in these slacks. Sparcely distributed along the fringes of these slacks are *Bulbostylis barbata, Phyla nodiflora, Cyperus arenarius* and *Cyperus stoloniferus.*

In the depressions without surface water in the dry season, strand creepers like *Ipomoea pes-caprae, Tylophora indica, Phyla nodiflora, Pergularia daemia* and *Cissus quadrangularis* associated with *Eragrostis coarctata, Cyanotis fasciculata, Fimbristylis dichotoma* and *Sida veronicifolia* can be seen quite commonly. The raised ridges are colonised by *Launaea pinnatifida* and *Ipomoea pes-caprae.* With the increasing height and dryness, the surrounding sand dunes are occupied only by *Spinifex littoreus.* One slack near the starting point of Rameswaram Road on the side of Rameswaram village containing water with a very high degree of salinity and smelling of sulphurated hydrogen supports no vegetation. On a little raised level on the periphery of the slack, however, *Ipomoea pes-caprae* and *Cyperus stoloniferus* forming a mat can be seen, probably as a result of decreased salinity there.

MATERIALS AND METHODS

To investigate the chemical composition of the soluble salts in waters of dune slacks, water samples were collected from the following sites during mid-September of 1961:

(i) Ground water at about 45 cm depth from the slack in between the parallel lines of mobile sand dunes facing the sea (Water sample No. 3)

(ii) Ground water at about 52 cm depth from the slack surrounded by consolidated sand dunes behind the lines of mobile sand dunes (Water sample No. 4)

(iii) Ground water at about 30 cm depth from the slack in between the consolidated sand dunes on the left side of Pamban to Rameswaram Road Rly. line at a distance of 1.5 km from Pamban (Water sample No. 10)

(iv) Ground water at about 30 cm depth from the slack surrounded by consolidated sand dunes on the left side of Pamban to Rameswaram Road Rly. line at a distance of 2.5 km from Pamban (Water sample No. 11)

(v) Ground water at about 40 cm depth from the slack near the starting point of Rameswaram Road on the side of Rameswaram village (Water sample No. 5)

A few well water samples representing the area and samples of sea water were also collected for comparison purposes and finding out the influence of sea water if any on the waters of slacks as well as wells.

The water samples were analysed by the standard methods outlined below and the data in milli-equivalents/litre in respect of ionic composition of water samples are set out in tables I—III.

Determinations of pH were made calorimetrically and total dissolved solids were estimated gravimetrically be the method of A.O.A.C. (1950). Chlorides were estimated by titration of an aliquot of water sample against standard $AgNO_3$ solution using K_2CrO_4 as an indicator and carbonates and bicarbonates by titrating an aliquot against $N_{20}H_2SO_4$, using phenolphthalein and methyl orange as indicators by the methods described by Jackson (1958). Sulphates were estimated gravimetrically as $BaSO_4$ (Scott 1939). Calcium estimations were made volumetrically by the method of Hillebrand and Lundell (1929). Magnesium was determined by precipitation with lime water and back titrating the excess of lime water against standard acid solution as described by Scott (1939). Sodium and potassium were estimated by the determination of combined weights of their chlorides and total chlorine and consequent calculation of two ions individually by the method devised by Division of Soils, University of Nebraska and described by Jackson (*loc. cit.*)

RESULTS

pH: The pH values of water samples from slacks ranging between 7.6→9.5 indicate that they are alkaline. The highest pH value of 9.5 is of a water sample with an extraordinary high degree of salinity, which is quite different in ionic composition also from the other water samples.

Total dissolved solids: Total soluble salts are very high and range between 690–1610 ppm. (average 1025 ppm.), leaving aside water sample No. 5, which contains extraordinarily high dissolved solids to the extent of 25620 ppm.

Sodium and Chloride: Sodium ions range between 4.31-11.85 milliequivalents/litre (average 7.62 m.e./litre) and chloride ions vary between 2.83–11.79 m.e./litre (average 7.59 m.e./litre); water sample No. 5 however contains 374.70 m.e./litre of sodium and 293.21 m.e./litre of chloride. The two ions are present almost in equivalent amounts with the exception of samples Nos. 3 and 5 where Na/Cl ratios are 1.52 and 1.28 respectively.

Calcium and bicarbonate: The chief source of these two ions must be the shell fragments present in abundance in the soils of the area. However, it is interesting to note that Ca^{++} ions ranging between 1.42-1.60 m.e./litre (average 1.50 m.e./litre) are far from being equivalent to the bicarbonate ions ranging between 3.00-8.10 m.e./litre (average 4.88 m.e./litre). Next to K^+ ions Ca^{++} ions are the least abundant. Ca^{++} ions are of the extent of 0.80 m.e./litre only in comparison to the high concentration of 58.2 m.e./litre of HCO_3^- ions and 31.00 m.e./litre of CO_3^{--} ions in sample No. 5.

Potassium: This ion is the least abundant among the four metallic cations and ranges between 0.24-0.75 m.e./litre (average 0.41 m.e./litre), with the exception in sample No. 5 where it is to the extent of 12.2 m.e./litre and more in concentration than Ca^{++} and Mg^{++} ions. The chief sources of this ion may be felspar particles present in the soils and sea water.

Magnesium: Soluble magnesium is very high in these samples ranging between 3.40-9.60 m.e./litre (average 5.58 m.e./litre) with the exception of sample No. 5, where it is only 5.60 m.e./litre as compared with the total dissolved solids 25620 ppm. High magnesium contents suggest the influence of sea water on the waters in the slacks.

Sulphate: This ion is also appreciably high although generally less than Mg^{++} ions concentration. This ion ranges between 1.51-4.42 m.e./litre (average 2.90 m.e./litre). In sample No. 3, SO_4^{--} ions are a little higher than Mg^{++} ions whereas in sample No. 5, SO_4^{--} ions are much higher than the Mg^{++} ions.

Carbonate: Either there are no carbonate ions or these are in negligible concentration in these water samples. Water sample No. 5, however, is an exception in respect of the content of carbonate ions also and contains 21.0 m.e./litre of the same.

DISCUSSION

The waters from these dune slacks are distinctly alkaline, rich in all the ions excepting CO_3^{--}. Amongst the metallic ions, K^+ is the least abundant, next in order being Ca^{++}. Comparison of the analyses of dune slack water samples (Table I) with the well waters of the area (Table II), sea waters (Table III) and world average fresh water (Data from Conway 1942) [Averages of different types of water samples are presented in Table IV],

TABLE I

Chemical composition of dune slack water samples from Rameswaram Island

Water sample No.	Location	Depth from ground level in cm	pH (aerated)	Total dissolved solids (ppm.)	Milli-equivalents/litre								Na/Cl ratio	Mg/Cl ratio	Ca/HCO$_3$ ratio
					CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	Ca^{++}	Mg^{++}	Na^+	K^+			
3	Slack in between the lines of mobile dunes facing the sea	45	8.4	690	traces	3.00	2.83	4.15	1.60	3.40	4.31	0.24	1.52	1.20	0.53
4	Slack surrounded by consolidated sand dunes behind the lines of mobile sand dunes	52	7.8	1610	—	8.10	11.79	4.42	1.50	9.60	11.85	0.75	1.01	0.81	0.19
10	Slack in between the consolidated sand dunes on the left side of Pamban to R. Road Rly. line at a distance of 1.5 km from Pamban	30	7.6	880	—	4.20	7.81	1.51	1.42	4.40	7.03	0.34	0.90	0.56	0.34
11	Slack surrounded by consolidated dunes on the left side of Pamban to R. Road Rly. line at a distance of 2.5 km from Pamban	30	7.6	920	—	4.20	7.92	1.54	1.48	4.90	7.28	0.31	0.92	0.62	0.35
	Mean		7.9	1025	—	4.88	7.59	2.90	1.50	5.58	7.62	0.41	1.09	0.80	0.35
*5	Highly saline water slack near the starting point of R. Road on the side of Rameswaram village	40	9.5	25620	31.00	58.20	293.21	23.74	0.80	5.60	374.70	12.20	1.28	0.02	0.02

* This slack containing water with an extraordinary high degree of salinity and different in ionic composition from waters of other slacks is being dealt separately.

TABLE II

Chemical composition of water samples from wells in Rameswaram Island

Water sample No.	Location	Depth from ground level in cm	pH (aerated)	Total dissolved solids (ppm.)	Milli-equivalents/litre CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	Ca^{++}	Mg^{++}	Na^+	K^+	Na/Cl ratio	Mg/Cl ratio	Ca/HCO$_3$ ratio
9	Well near Pamban bridge on way to Kundukal point	120	8.2	825	—	4.10	6.89	1.35	2.20	3.90	5.74	0.59	0.83	0.57	0.54
8	Well off Rameswaram to Thangachimadam Rly. line at a distance of 4 km from Rameswaram	210	7.8	630	—	4.50	2.75	1.34	2.10	1.20	4.84	0.32	1.76	0.44	0.47
*12	Well in the north of Rameswaram village at a distance of 1.5 km from Rameswaram	300	8.3	3050	—	10.40	30.55	6.86	4.20	14.00	27.63	1.30	0.90	0.46	0.40
6	Well in the Research Garden opposite Rameswaram Road Rly. Station	140	9.1	380	0.60	1.10	2.02	2.10	1.00	2.40	2.18	0.25	1.08	1.19	0.91
	Mean		8.3	1241	0.15	5.02	10.55	2.91	2.38	5.37	10.10	0.62	1.14	0.67	0.58

* This well water although comparatively richer in dissolved solids than the other well waters, is dealt along with these as it is similar to them in many other respects.

TABLE III

Chemical composition of sea water samples

Water Sample No.	Location	pH (aerated)	Total dissolved solids (ppm.)	Milli-equivalents/litre CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	Ca^{++}	Mg^{++}	Na^+	K^+	Na/Cl ratio	Mg/Cl ratio	Ca/HCO$_3$ ratio
2	Sea water from near Pamban bridge	8.2	38485	—	2.70	581.44	63.39	22.80	111.20	498.27	12.97	0.86	0.19	8.44
7	Sea water from Dhanushkodi Shore	8.1	36060	—	2.70	554.63	57.15	21.60	123.60	437.58	10.31	0.79	0.22	8.00
	Mean	8.2	37273	—	2.70	568.04	60.27	22.20	117.40	467.90	11.64	0.83	0.20	8.22

TABLE IV

Average chemical composition of slack waters, well waters, sea water and fresh water

Water type	pH (aerated)	Total dissolved solids (ppm.)	Milli-equivalents/litre CO_3^{--}	HCO_3^-	Cl^-	SO_4^{--}	Ca^{++}	Mg^{++}	Na^+	K^+	Na/Cl ratio	Mg/Cl ratio	Ca/HCO$_3$ ratio
Rameswaram, four slack waters	7.9	1025	—	4.88	7.59	2.90	1.50	5.58	7.62	0.41	1.09	0.80	0.35
Rameswaram, saline slack water	9.5	25620	31.00	58.20	293.21	23.74	0.80	5.60	374.7	12.20	1.28	0.02	0.02
Rameswaram, four well waters	8.3	1241	0.15	5.02	10.55	2.91	2.38	5.57	10.10	0.62	1.14	0.67	0.58
Sea Water	8.2	37273	—	2.70	568.04	60.27	22.20	117.40	467.90	11.64	0.83	0.20	8.22
* World average fresh water			—	1.71	0.23	0.37	1.49	0.42	0.36	0.08	1.57	1.83	0.87

* Data from Conway (1942)

will bring out certain points of interest. As expected the concentration of Ca^{++} ions in the water samples from the slacks surrounded by sand dunes abundant in shell fragments is not high and it is clearly evident that calcium is far from being equivalent to bicarbonate, the average ratio of Ca/HCO_3 being in fact only 0.35, as against 0.58 in well waters, which is also quite low, 8.22 for sea water and 0.87 for world average fresh water. The ratio of Na/Cl (1.09) is comparable to well waters (1.14) but is higher than the sea water (0.83) and lower than the world average fresh water (1.57). Similarly the ratio of Mg/Cl (0.80) for the slack waters as against 0.67 for well waters is much higher than this ratio for sea water (0.20) and much lower than the ratio (1.83) for world average fresh water. From the above it may be concluded that the ionic composition of dune slack waters is more or less similar to the well waters of the area but very much different from the sea water and fresh water. The explanation of these anomalies in the slack & well waters probably lies in the operation of ion-exchange processes. It was Hissink (1907), who pointed out that base exchange was probably involved in the so called "Kwelders" along the coast of Holland (Soils subjected to overflow by sea water at high tide). Normal soils contain but little exchangeable Na^+ and K^+ as the monovalent bases are less strongly adsorbed than divalent Ca^{++} and Mg^{++}. This is especially true of Na^+. Should Na^+ become adsorbed—that is, exchangeable—at any stage in the normal process of soil formation, under a humid climate it will be replaced sooner or later to a high degree by other cations, which pass into solution as a result of weathering or H^+ ions of biological origin.

As a result of the action of sea water, Hissink (1935) further observed that the "Kwelder" soils along the coast of Holland contain abnormal proportions of exchangeable Mg^{++} and Na^+; but after flooding by the sea is prevented by endykment, weathering and leaching by rain water bring about rapid replacement of exchangeable Na^+ by Ca^{++} derived from $CaCO_3$ of the soil. Later the greater part of the exchangeable Mg^{++} is also replaced by Ca^{++} or H^+ ions, thus creating in the outside solution an excess of Na^+ and Mg^{++} ions in comparison with Cl^- ions. Ion-exchange processes similar to the soils along the coast of Holland appear to have taken place in soils of Rameswaram Island. Gorham (1958 loc. cit.) has also pointed out similar ion-exchange processes in soils from Blankeney-Point in Norfolk. Consequently much of the adsorptive capacity of the soil materials of Rameswaram island is probably saturated by Na^+ and Mg^{++} ions supplied in considerable quantities by sea spray and sea water seepage. But when shell fragments present in abundance in the area dissolve in percolating rain water, the calcium of the shells displaces some of the sodium and magnesium from the adsorbed phase and creates in the outside solution an excess of these two ions in relation to chloride and a deficiency of calcium in relation to bicarbonates. It seems that the sub-soil, which feeds these slacks partially, is recharged with sea salt to some extent by the cyclical rise of the tide and the same is known to have a marked influence upon the level of the fresh water table in the dunes (Hill & Hanley 1914). Further it will be of considerable interest to know that base-exchange plays an exceptionally important role in the alkali soils of dry regions also (Gedroiz 1912). Such ion exchanges are also well known in arid alkali soils of Solonetz type (cf. Robinson 1949), which, however, exhibit very different physical properties owing to their much finer textures and indeed commonly possess very distinctive characteristics.

The source of K^+ in these waters is either potassium leached down by rain water after decomposition of felspar particles in the soils, of sand dunes or sea water spray and sea water seepage through the soil. Sulphates may also be there due to the influence of sea water. It may, therefore, be inferred that sea water has a marked influence upon the fresh water in the slacks not only in the form of sea spray but by the cyclical rise of tide also.

The ionic composition of water from the highly saline water slack is quite different from the composition of waters from other slacks, wells, sea and fresh water. It contains a very high proportion of CO_3^{--} ions (31.0 m.e./litre) as well as HCO_3^- ions (58.2 m.e./litre). Although the ratio of Na/Cl (1.28) is appreciably high, the ratios of Mg/Cl (0.02) and Ca/HCO_3 (0.02) are very low. As the water in the slack smelled strongly of H_2S, it appears that Na_2CO_3 has been formed by the bacterial reduction of Na_2SO_4. Instances of Na_2CO_3 formations in certain places in the Nile Delta by sulphate reducing bacteria have been furnished by Garcie *et al.* (1934). Eaton (1935) has also suggested that sulphate reduction might have taken place in the sub-soils of the San Joaquin valley, California. The higher concentration of salts may be due to excessive flooding of the slack by sea water.

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