PART –B

Geochemical study of the Sambhar lake

Chapter 5

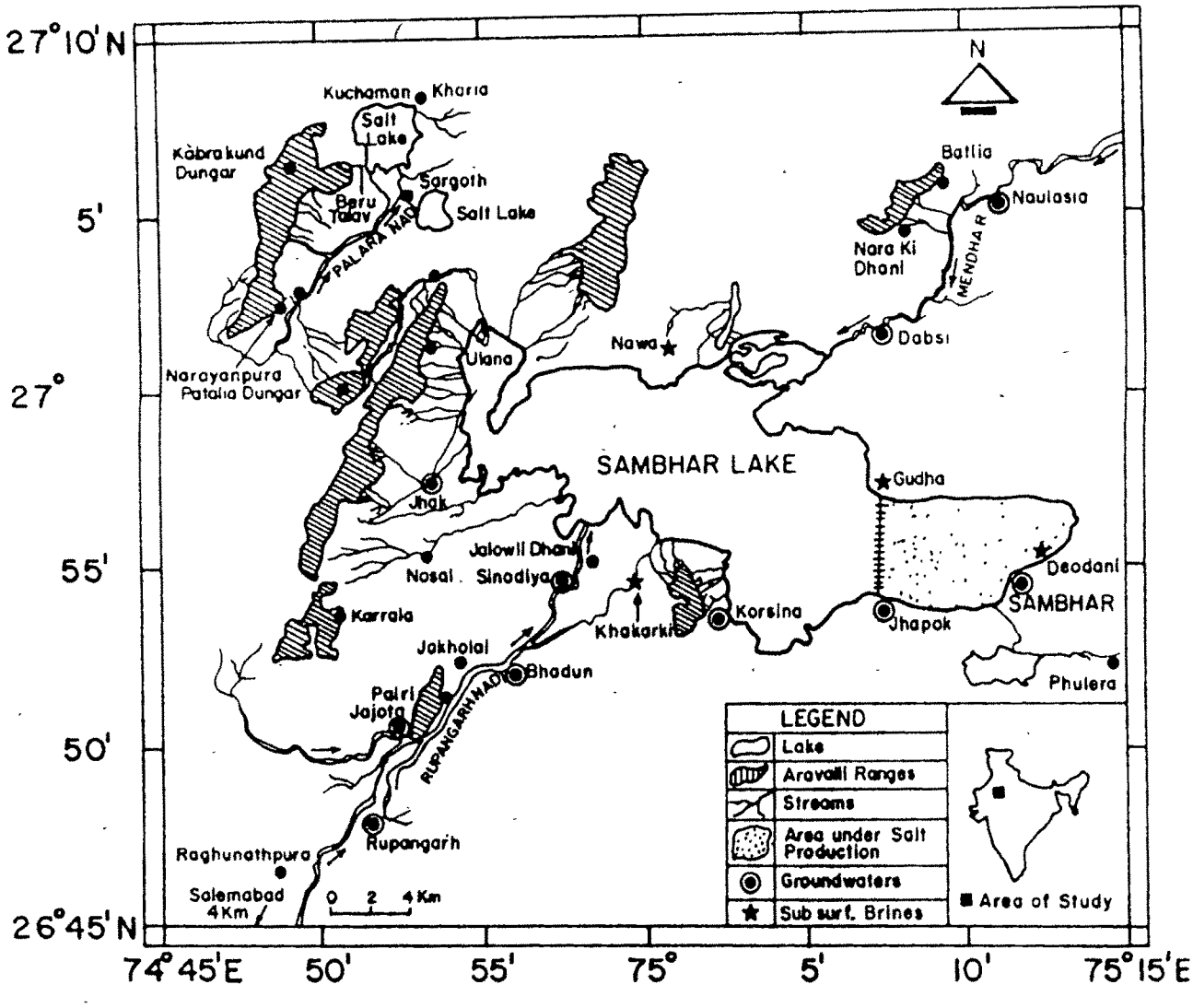
Introduction

Rajasthan state, in the Thar desert of India is endowed with a large number of saline lakes notably the Sambhar, Didwana, Kuchaman, Lunkaransar and the Pachbhadra. These lakes are shallow and ephemeral. Among these, the Sambhar lake, situated at $26^0 52'-27^0 2'$N, $74^0 53'-75^0 13'$E, is the largest with an area of $\sim$ 225 km^2 (Fig. 5.1). It is a closed sedimentary basin which is reported to have been formed by neotectonism (Deshmukh and Rai,1991) and aeolian activity as the lake boundary is bounded by wind-blown sand-dunes. About 2 $\times 10^5$ tons of NaCl is manufactured annually from the Sambhar lake waters and shallow sub-surface brines in its basin. The origin of salt in the lake basin has been a subject of scientific interest during the recent years. The various hypotheses proposed include: (i) dissolution of salt from halite beds (relict of Tethys sea) within the basin (Godbole,1952) (ii) weathering of country rocks followed by evaporation (Aggarwal,1951) and (iii) aeolian transport of salt laden aerosol particles from the Gulf of Kutch by SW monsoon winds (Holland & Christie,1909). Of these, the first two can be grouped under "internal" and the third as an "external" source of salt. A comprehensive review on the sources of salt in the Sambhar lake is given by Biswas et al (1982).

5.1 Geology, Hydrology and Climate of the Sambhar lake

For better understanding of the evolution of saline lakes and brines, relevant information on local climate, hydrology, sedimentation history and tectonics are very helpful.

Figure 5.1: Map showing the sample locations in and around the Sambhar lake. The groundwater wells are indicated by encircled point ◉ and sub-surface brine wells are shown by asterik symbol ($\star$). Shallow groundwater samples from the river bed are taken to be representative of river waters. In the figure, major village sites for location of groundwaters and some of the salt producing sites for sub-surface brine wells are also shown, however, additional samples were also collected at a distance of 50–100 m from those marked locations. The map also describes important geomorphic features of the lake area.


27°10'N
5'
27°
55'
50'
26°45'N
74°45'E
50'
55'
75°
5'
10'
75°15'E
N
Kuchaman
Kharia
Salt Lake
Kabrakund Dungar
Beru Talav
Sargoth
Salt Lake
PALARA NAD
Narayanpura Patalia Dungar
Ulana
Nawa
Batlia
Naulasia
Nara Ki Dhani
MENDHA R
Dabsi
SAMBHAR LAKE
Gudha
Jhak
Jalowli Dhani
Nosal
Sinodiya
Karrala
Khakarki
Korsina
Jhapok
Deodani
SAMBHAR
Jakholai
Bhadun
Phulera
Palri
Jajota
RUPANGARH NAD
Rupangarh
Raghunathpura
Salemabad 4Km
0 2 4Km
LEGEND
Lake
Aravalli Ranges
Streams
Area under Salt Production
Groundwaters
Sub surf. Brines
Area of Study

The Sambhar lake is located at an elevation of 360 m above the Mean Sea Level. The lake is underlain by Pre-Cambrian basement rocks, predominantly consisting of schiests, phyllites and quartzites. The crystalline basement is overlain by Quaternary clays and silts (Aggarwal, 1951). The base of the Quaternary sedimentary column is made of fluvial deposit of alluvial sand and clays indicating humid climatic condition in the past. The lake basin is surrounded by windblown high terraces of sand and clay. In the present-day geohydrologic set-up, the principal source of water to the lake is local precipitation and drainage from the catchment. The catchment area ($\sim$ 5600 km^2, Biswas et al,1982) of the lake has small and large streams e.g. Roopangarh, Mendha, Kharian and Khandel (Aggarwal,1951), however, their supply of water to the lake is limited because of aeolian activity in the region and man-made dams constructed for irrigation purposes. Of these rivers, currently only the Roopangarh and the Mendha seem to supply water to the lake (Fig. 5.1), and flow in these streams is highly seasonal and occurs only for a few days during the SW monsoon (June–September). These rivers drain mainly through Pre-Cambrian schists, phyllites and slates. From the field observation, it is evident that water table of the adjacent groundwaters is generally 5–10 m above the lake bed. However, at places within the river basin (for example near Roopangarh town), groundwaters are available at 20–30 m above the lake bed. This indicates a significant hydraulic gradient that favours the groundwaters flow towards the lake basin in addition to the surface run-off during the monsoon season. The groundwaters of this region show considerable variations in their salinity, among these the low salinity waters are used for irrigation and domestic purposes.

Climatic data from the three meteorological stations (Jaipur, Sikar and Ajmer) close to the Sambhar lake show that January is the coldest month with minimum temperature of about 6 – 8^{0}C and May is the hottest month with maximum temperature ranging between 39 – 41^{0}C. The maximum average relative humidity during the monsoon season is about 76% in the month of July and minimum of about 15–20% during summer months before the onset of monsoon. Information on wind regime indicates that the diurnal average speed varies from 4 to 12 kmph (Mar–July) and minimum being at 2–3 kmph during the winter (Dec–Feb). The lake receives an average annual rainfall of 50 cm and is characterized by evaporation almost balancing the inflow. As a result, Sambhar represents

a seasonal lake with water drying up almost completely during the hot and dry summer months and getting replenished during the monsoon.

Changes in climatic conditions during the recent past have also influenced the geomorphic evolution of the Thar desert and its associated features. The stratigraphic and radiocarbon chronologies of the three lake basins in the Thar desert namely the Sambhar, Didwana and Lunkaransar and the proxy records contained in them indicate similar climatic conditions over the region (Sareen,1952; Singh et al,1972; Wasson et al,1984). These studies show that prior to 13 ka BP the lake condition was hypersaline; around 10 ka BP the lacustrine deposition (laminated clay) started and continued up to 4.5 ka BP and between 4.5 ka BP to the present the environment was generally semi-arid. In addition, variation in paleomonsoon in this region has been studied based on palynology (Bryson and Swain,1981; Swain et al,1983) which indicate sub-humid phase between 10.5–3.5 ka BP. Swain et al (1983) postulated Sambhar lake's paleolevel (based on hydrologic balance and radiation budgets) to be about 20 m above the present value during 10.5–3.5 ka BP. Furthermore, geomorphic evidences e.g. dry river beds and paleo river channels (Allchin et al, 1978; Ghose, 1964) have indications to stronger monsoon rainfall in the past compared to the present. It appears that with the onset of aridity in the region, the river tributaries were dried and some of them were buried under sand by aeolian activity. Preliminary studies on salinity of the Sambhar lake have not evidenced presence of solid evaporite deposits in the lake basin (Aggarwal,1951; Mishra,1982). In the absence of thick-evaporite deposits, the shallow hypersaline brines below the lake bed is considered to be due to paleoclimatic transition from wet to dry phases (Mishra,1982).

5.2 Present-day lake configuration

Currently salt (NaCl) is being manufactured extensively from the lake water and sub-surface brines by solar evaporation. The eastern side of the lake, occupying an area of 71 km^2 (Fig. 5.1) is at present isolated from the main reservoir by an embankment (a railway track in the figure). In this configuration, the main reservoir of the lake, therefore, is left with an effective area of 154 km^2. The isolated area (71 km^2) is utilized for salt production by pumping of waters both from the lake and shallow sub-surface brines. The sub-surface

brines which occur generally at 3 to 4 m depth below the lake bed are the principal source of salt. At some places viz. Khakarki, Sinodiya and Nawa on the periphery of lake, these brines are available even at deeper depths ranging from about 40 to 80 m mainly due to the topographic highs. On the lake bed the salt producing network consists of small to large size evaporating reservoirs, pans/kyars and areas for disposing the residual liquor of the brine i.e. the bittern [1].

Goals of the Present Study

Earlier studies on the various saline lakes in Rajasthan (Aggarwal,1951; Biswas et al,1982; Bhattacharya et al,1982; Mishra,1982; Deshmukh and Rai,1991) were mainly to evaluate their potential for commercial exploitation, though some attempts were made to speculate on the sources of salt to these lakes. In this work a detailed geochemical and isotopic study of various hydrologic systems of the Sambhar lake has been made in different seasons to obtain information on the evolution of surface and sub-surface brines and the inter-relation between them. The specific objectives of this study are:

(i) to determine the chemical and isotopic composition of the source waters, lake waters and sub-surface brines;

(ii) to simulate and model the annual evaporation cycle of the lake water and brines;

(iii) to place constraints on the possible source of salt to the lake;

(iv) to derive information on the abundances and behaviour of U–Th series nuclides in waters over wide range of salinities.

Chapter 6 describes the experimental techniques used in this study, Chapter 7 the results and discussion and Chapter 8 the summary of the present work.

[1]Bittern refers to the residual brine remaining after NaCl recovery, its major component being NaCl (~75%), Na_2CO_3 and Na_2SO_4.

Chapter 6

Experimental Techniques

The groundwaters, lake waters and sub-surface brines were sampled during different seasons (Feb 92–Oct 93) whereas water samples from the river basin were collected mainly during Oct 1993. Most of the sub-surface brine wells sampled are open wells dug in the lake bed for salt production. These wells are accessible for sampling only during Oct to June when salt production is being carried out. Also, the salt producing networks e.g. evaporating pans, kyars and bitterns were sampled. In the following sections the techniques used in field and laboratory analyses are described. The lake waters and sub-surface brine samples were analyzed (see Appendix–B, Table 1B) for oxygen isotope ratio ($^{18}O/^{16}O$) and major dissolved ions. In addition, U–Th series nuclides e.g. uranium isotopes, radium isotopes ($^{226,228}Ra$), ^{210}Po and ^{210}Pb were measured with a view to understand geochemical behaviour of these nuclides over a wide range of salinities and to use some of them as natural tracers to infer the source of salt to the lake.

6.1 Measurement of oxygen isotope ratios

The ($^{18}O/^{16}O$) ratio, expressed conventionally as $\delta^{18}O$, of water samples was measured by the CO_2 equilibration method (Epstein and Mayeda,1953). The $\delta^{18}O$ is defined as:

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{Sample}}{(^{18}O/^{16}O)_{Std}} - 1\right] \times 10^3 \qquad (6.1)$$

and expressed in parts per thousand or per mil ($^0/_{00}$). The standard refers to the Standard Mean Ocean Water (SMOW) supplied by IAEA, Vienna having isotopic ratio $^{18}O/^{16}O$ of $\sim 2000 \times 10^{-6}$.

In brief, 2 ml of water sample was taken in a glass bottle (approximately 8 ml capacity) and treated with 1 drop of 100% orthophosphoric acid to decompose the carbonates and liberate CO_2. The acid treated samples were repeatedly frozen (three times) with liquid nitrogen and evacuated to pump out the dissolved gases. This process was carried out each time by thawing and refreezing at liquid nitrogen temperature (-196^0C). After this, high purity CO_2 gas from a tank was let into the glass bottles containing the sample to a pressure of $\sim$ 8 cm, and water and CO_2 allowed to equilibrate. In order to achieve complete isotopic equilibration between CO_2 and H_2O, the bottles were kept in a water bath at a constant temperature of 25^0C for 48 h. The isotopic exchange between CO_2 and water molecules takes place as:

$$\frac{1}{2}C^{18}O_2 + H_2^{16}O \rightleftharpoons \frac{1}{2}C^{16}O_2 + H_2^{18}O \tag{6.2}$$

Later, the CO_2 was extracted and purified for $^{18}O/^{16}O$ ratio measurement using a VG Micromass 903 mass-spectrometer. Four samples and a laboratory standard were measured in a batch. The $\delta^{18}O$ measured in fresh water replicate samples showed a precision of ± 0.1 $^0/_{00}$ whereas for brines, the reproducibility was found to be $\pm$ $0.3^o/_{oo}$ (1σ). As the brines analyzed for $\delta^{18}O$ are NaCl type with trace concentrations of Ca and Mg ions, the salt-effect on the ^{18}O fractionation is assumed to be negligible (Gat,1981c). For detailed experimental procedure with PRL's set-up of CO_2 equilibration system, cross-calibration of the laboratory standard with respect to V-SMOW and correction involved in measurement of oxygen isotopic ratio ($^{18}O/^{16}O$) for water samples reference is made to Krishnamurthy (1984).

6.2 Major ion determination

The water samples were filtered using Gelman cartridge (pore size 1μm) for major ions determination, however, measurements of pH and alkalinity were done on unfiltered samples at site within a few hours of sampling. The pH was measured using a portable digital pH meter with a precision of ± 0.1 units and total alkalinity (defined as eqv. sum of HCO_3^- and CO_3^{2-} ions) by titrating the water samples with 0.02/0.2N HCl in presence of methyl orange as indicator. The precision of alkalinity measurement, based on repeated titra-

tion of the standard Na_2CO_3 and sample solution with 0.2N HCl, was found to be ±5%. The filtered water samples were analyzed for major ions (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-,SO_4^{2-}) by the Atomic absorption spectrophotometry (AAS) and ion chromatography. The coefficient of variation for Na and Cl ions, 2.6 and 2.2% respectively, was calculated using eqn.(2.1) (see p. 14) as a measure of precision of measurement. In a few samples, Cl estimation was done using both $AgNO_3$ titrimetry and ion-chromatography method (Table 6.1). The mean reproducibility of Cl measurement by these two independent methods was found to be better than 2%.

Table 6.1 : Reproducibility of chloride measurement by two different methods

Sample	Cl(meq/l)	
	(a)	(b)
SL #10	24.5	23.9
SL #21	19.6	18.2
SL #24	63.7	65.3
SL #44	455	445
SL #48	75.2	76.6
SL #50	23.8	22.7
SL #62	19.2	18.7
SL #77	3922	4046

(a) based on $AgNO_3$ titration, and
(b) based on ion-chromatography method

The concentration of sulphate in the brine samples was determined gravimetrically by precipitating $BaSO_4$ from the samples. Repeat measurements of SO_4 in a few samples showed reproducibility within 1%. For all groundwater samples, SO_4 was estimated by ion-chromatography with a precision of 3%.

The charge balance between Σcations and Σanions for 86 samples is 0.98±0.06. These data are shown in Fig. 6.1.

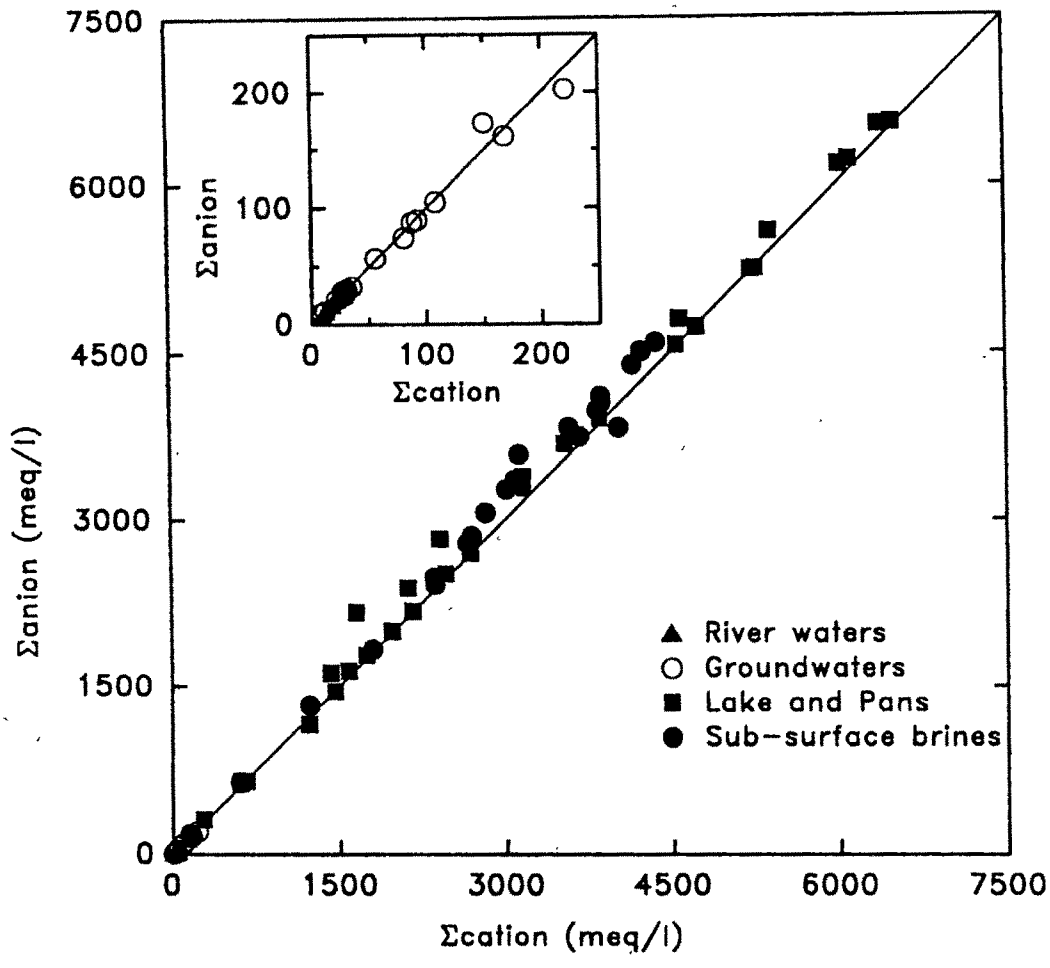


Figure 6.1: Scatter diagram of Σcations and Σanions in water samples from the various reservoirs in and around the Sambhar lake. Most of the data lie on the "equiline" indicating that the ions other than those measured in this study do not contribute significantly to the charge balance. The inset in the figure is for groundwaters and river waters.

6.3 Radionuclide measurements

For radioisotope (U, Po, Pb) measurements in groundwaters and river waters, preconcentration from $\sim 10-20\ \ell$ filtered and acidified samples was done in the field using $Fe(OH)_3$ precipitation in presence of U–Po–Pb yield tracers viz. ^{232}U, ^{209}Po and Pb-carrier (Krishnaswami et al,1982; Sarin et al,1992). The $Fe(OH)_3$ containing U, Po and Pb was dissolved in HCl and these nuclides were separated following the techniques routinely employed in our laboratory for seawater analysis (Sarin et al,1992). For brine samples, it was difficult to filter through either millipore or Whatman filter papers due to the presence of algae. Under such a condition, U, Po and Pb isotopes were determined in unfiltered smaller volume of samples (for U, 25–250 ml and for Po/Pb, $\sim 5\ \ell$) by drying and digesting with nitric acid in presence of their yield tracers. Such a scheme was followed to ensure spike equilibration with the natural isotopes in water samples. The purified U, Po and Pb (via Po) samples were α assayed to determine their concentrations. The chemical yield for uranium in groundwaters centered around 75% whereas in the brines the range was between 30–80%. For the two other radionuclides, ^{210}Po and ^{210}Pb, the chemical yield in groundwaters was observed to be around 70% and in brines the range was between 40–60 %.

The Ra isotopes ($^{226,228}Ra$) were measured by preconcentrating them on MnO_2 fibre (Moore,1976). The Mn fibre containing the Ra isotopes was brought to the laboratory, treated with 3M HCl ($\sim$ 250 ml), warmed, filtered and the acid solution transferred to a Rn flask. The ^{226}Ra was measured in the solution via ^{222}Rn (Mathieu, 1988). For this, sample solution in the Rn flask was purged with pure He gas, sealed and stored for radon to grow for about two weeks. The ^{222}Rn was purged out with He, purified and counted using scintillation counters. The efficiency of extraction and counting was ascertained using ^{226}Ra standards. The standards and blanks were periodically analyzed to check the measurement of ^{226}Ra. After the ^{226}Ra determination, $BaSO_4$ was precipitated from the sample solution, dried and sealed in a vial for γ-assay through a low background HPGe well detector coupled with multichannel analyzer. Based on the $^{228}Ra/^{226}Ra$ ratio, derived from the γ-ray spectra and concentration of ^{226}Ra determined by the radon method, the activity of ^{228}Ra was calculated.

The errors given in all the above radionuclide determinations correspond to $\pm 1\sigma$,

calculated from counting statistics and uncertainty of tracers/spikes calibrations and blank corrections.

In the following chapter, the results on the isotopic composition of oxygen, major ions and radionuclide are discussed. Major ion concentrations are reported in meq/l and those of radionuclides in (μg or dpm)/kg. All ion ratios in the following chapter refer to equivalent ratios.

Chapter 7

Results & Discussion

Chemical and isotopic analysis of the major water reservoirs in and around the Sambhar lake has been made with a view to evaluate possible relationships between them and to study the chemical evolution of the lake. The chemical and isotopic composition of continental waters is influenced by several factors such as chemical weathering of rocks, the composition of meteoric precipitation, mixing of various endmember waters, the process of evaporation and also biological activities. Groundwaters in granite and rhyolite terrains have compositions dominated by Na, HCO_3, SiO_2 and F ions whereas Ca, Mg and pH are generally low (White et al,1963). Similarly, groundwaters from sedimentary basins are characterized by low SiO_2 and high Ca, Mg and SO_4 ions. The chemistry of groundwaters is also influenced by dilution effect during recharge and dissolution of evaporite minerals formed in unsaturated zone especially in arid and semi-arid regions (Drever and Smith,1978). Using chemical data from California Sierra, Feth et al (1964) and Garrels and Mackenzie (1967) have shown that stream water chemistry is related to the chemistry of source rock and its mineral equilibria. Aquatic organisms often influence the concentration of many elements e.g. C, N, P, S, Ca, Cd etc. by metabolic uptake, transformation, storage and release (Stumm and Morgan,1981).

Among several environmental isotopes, ^{2}H, ^{18}O, ^{3}H, ^{3}He and ^{222}Rn are used widely in hydrological applications. The isotopes associated with water molecules i.e. ^{3}H, ^{2}H and ^{18}O are the ideal tracers; their spatial and temporal variabilities help to understand the origin of groundwaters on a regional scale, surface and groundwater interactions, lake water balance, leakage from water reservoirs, groundwater recharge, paleoclimates and mois-

ture circulation patterns etc. (Gat,1981a–c; Gonfiantini,1981; Fontes,1981; Payne,1981; Saxena,1987).

In this study, attempt has been made to understand the evolution of isotopic and chemical composition of the Sambhar lake waters based on the observations during annual wetting and drying cycles, mineral-aqueous equilibria, chemical weathering of surrounding rock formations and behaviour of some of the selected U-Th radionuclides in these waters over a wide range of salinity. These results are discussed in the following section.

7.1 Oxygen isotope evolution of the Sambhar lake and sub-surface waters

The oxygen isotope ratio ($^{18}O/^{16}O$) of natural waters exhibits a wide range due to isotopic fractionation processes which occur during chemical (e.g. isotopic exchange reaction) and physical processes (e.g. evaporation, condensation and gaseous diffusion). Therefore, along with the background information on environment and hydrological conditions, the variation in abundances of oxygen isotope ratio can help understand the physico-chemical processes operating in a hydrologic system. For this reason, isotopic composition of oxygen is frequently used to provide a better understanding of hydrological problems viz. identifying qualitatively and quantitatively the mixing proportion of various end-members of waters, characterization of aquifer systems and evaporation history of closed basin reservoirs.

Table 7.1: Oxygen isotope and major ion ratios in various water reservoirs in around the Sambhar lake (this study)

Reservoir	TDS range ($g.\ell^{-1}$)	$\delta^{18}O$ range ($^o/_{oo}$)	$\frac{Na}{Cl}$† (average)	$\frac{(Na+Cl)}{TDS}$ † (average)	$\frac{Cl}{SO_4}$ † (average)	$\frac{Alk}{(Ca+Mg)}$† range
Rain water	1.6 & 2.1*	−6.4 & −3.2	1.01	–	–	–
River water	0.5–1.8	−5.4 to −3.6	2.70	0.62	3.95	1.5–15
Groundwater	0.5–12.3	−6.5 to −3.0	1.03	0.71	11.62	0.2–4
Lake water	9.0–370	−5.5 to 24	1.08	0.94	12.19	4–1100
Evaporating pan	70–392	–	1.23	0.90	7.22	150–3900
Sub-surface Brine	70–270	−1.0 to 7.4	1.17	0.90	5.78	70–3000

* TDS (total dissolved solids) in $mg.\ell^{-1}$ † equivalent ratio

7.1.1 Oxygen isotopes in atmospheric precipitation, groundwaters and river waters

The $\delta^{18}O$ of the groundwaters collected from open wells (adjacent to the lake) ranges from -6.5 to -3.0 $^{o}/_{oo}$ and the TDS content is < 12.3 g/l (Table 7.1). Similar to groundwaters, the river water samples from the Mendha and Roopangarh (with TDS <1.8 g/l) show $\delta^{18}O$ variation from -5.4 to -3.6 $^{o}/_{oo}$. These results of $\delta^{18}O$ overlap with the values of two rain water samples, $-$ 6.4 and -3.2 $^{o}/_{oo}$, collected during July 1993. This observation, though based on a limited number of rain water samples, suggests that the $\delta^{18}O$ of the groundwaters along the periphery of lake is dominated by atmospheric precipitation.

In Figs. 7.1 the $\delta^{18}O$ values of the groundwaters are plotted against TDS for the samples collected during Oct (recharge period) and Feb months. These plots have been made to discern any relation between $\delta^{18}O$ and TDS which may provide information on the mixing trend among the groundwaters. The results for the Oct and Feb months show that the $\delta^{18}O$ of groundwaters around the Sambhar lake are within the range observed for rain water from the region. The differences in salt content among the various groundwaters could be attributed to varying amount of salt derived from weathering of their local recharge zones. An alternate explanation for the trend in the Figs. 7.1 is mixing of two endmembers, one endmember with low $\delta^{18}O$ and TDS and the other with high $\delta^{18}O$ and TDS. A similar inference has been made from the distribution of uranium isotopes in these groundwaters (detail discussion follows in later section on radionuclide systematics).

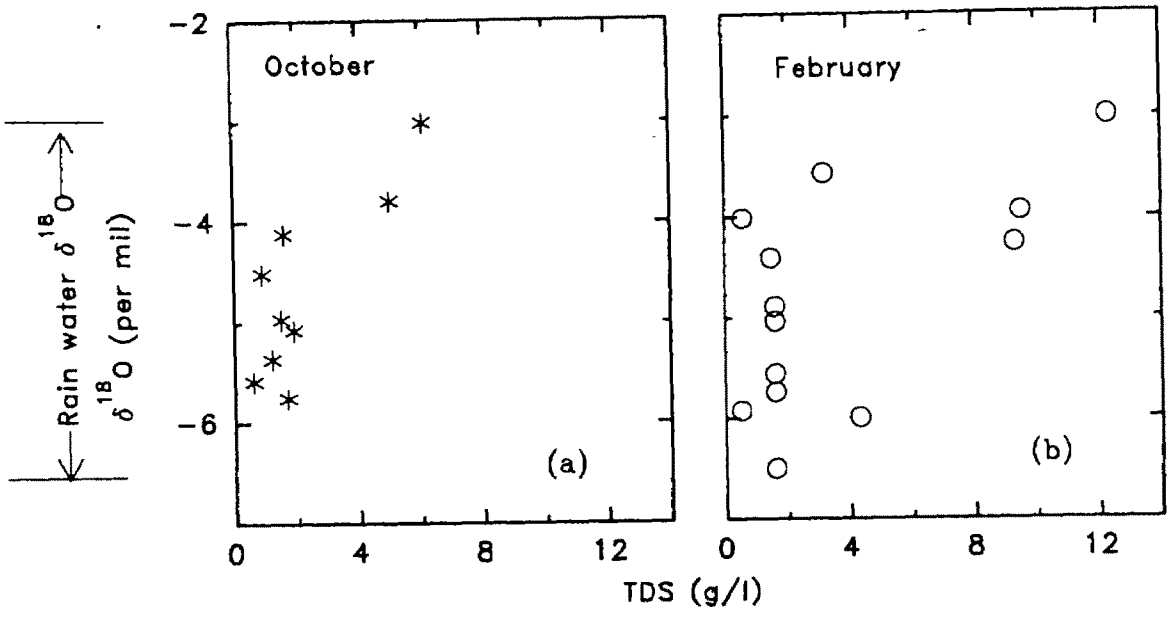


Figure 7.1: Scatter diagram of δ^{18}O vs. TDS for the Sambhar lake groundwaters collected during Oct and Feb months. The distribution of sample points collected during Oct. and Feb months essentially show two distinct group of groundwaters in terms of their salt contents. The δ^{18}O in these groundwaters are within the range of atmospheric precipitation.

The influence of evaporation on the groundwaters can be discerned through the δD$-\delta^{18}$O relationship. The evaporation generally causes a shift in the slope of δD$-\delta^{18}$O meteoric water line (MWL) (Dansgaard,1964). The MWL line (Craig,1961; Yurstsever and Gat,1981) defined as, δ D=(8.17$\pm$0.08) δ^{18}O + (10.56$\pm$0.64). In the present study, δD has not been measured but results of δD and δ^{18}O in groundwaters from the nearby region (Sambhar, Didwana and Kuchaman) show the following relation (Ramesh et al, 1993):

$$\delta D = 3.15 \ \delta^{18}O - 22.4 \qquad (n = 26) \tag{7.1}$$

A significant deviation in the slope of δD$-\delta^{18}$O line with respect to the MWL indicates the influence evaporation occurring in the groundwaters of this region.

7.1.2 Oxygen isotopes in lake, evaporating pans and sub-surface brines

With a view to understand better the chemical and isotopic relations between the lake water, the sub-surface brines which occur mostly 3–4 m below the lake bed, and the water in evaporating pans which is derived from the lake, water samples were analyzed for the measurement of major dissolved ions and oxygen isotopes in different seasons.

The lowest $\delta^{18}O$ value of $-5.5\ ^{0}/_{00}$ was measured during July 1992 when lake was recharged by precipitation. This value is within the range measured for rain and river waters (Table 7.1). The effect of evaporation is observed in subsequent months with the enrichment in both $\delta^{18}O$ and salt-content. The $\delta^{18}O$ shows a linear increasing trend up to a value of $\sim 20\ ^{0}/_{00}$ with the salt content (TDS) (Fig. 7.2a).

The $\delta^{18}O$ values and salt-content during July to April months show a strong positive correlation (r=0.91) both of them steadily increasing due to evaporation. At salinities exceeding $\sim$ 100 g/l (during May 93) there is a change in in the slope of the $\delta^{18}O$–TDS trend, the increase in $\delta^{18}O$ with TDS is much less in the salinity range 100–400 g/l, relative to that in the lower salinities, (9-100) g/l. During later stages of evaporation (TDS > 200 g/l), there is scatter in $\delta^{18}O$ values, cause of which is presently unclear.

Saturation in $\delta^{18}O$ during late stages of evaporation can be understood in terms of known models (e.g. Rayleigh and Craig–Gordon models) for $\delta^{18}O$ evolution trends in the lake basin. These models take into account processes such as evaporation and isotopic exchange between liquid and atmospheric water vapour. The oxygen isotope evolution in lake water over annual cycle of evaporation (July 92–May 93) is modelled using both Rayleigh and Craig-Gorden (1965) models. The Rayleigh eqn. used in modelling is (Gonfiantini,1981):

$$\delta = \delta_0 + 10^3 \cdot (1 - \alpha)\ lnf \qquad (7.2)$$

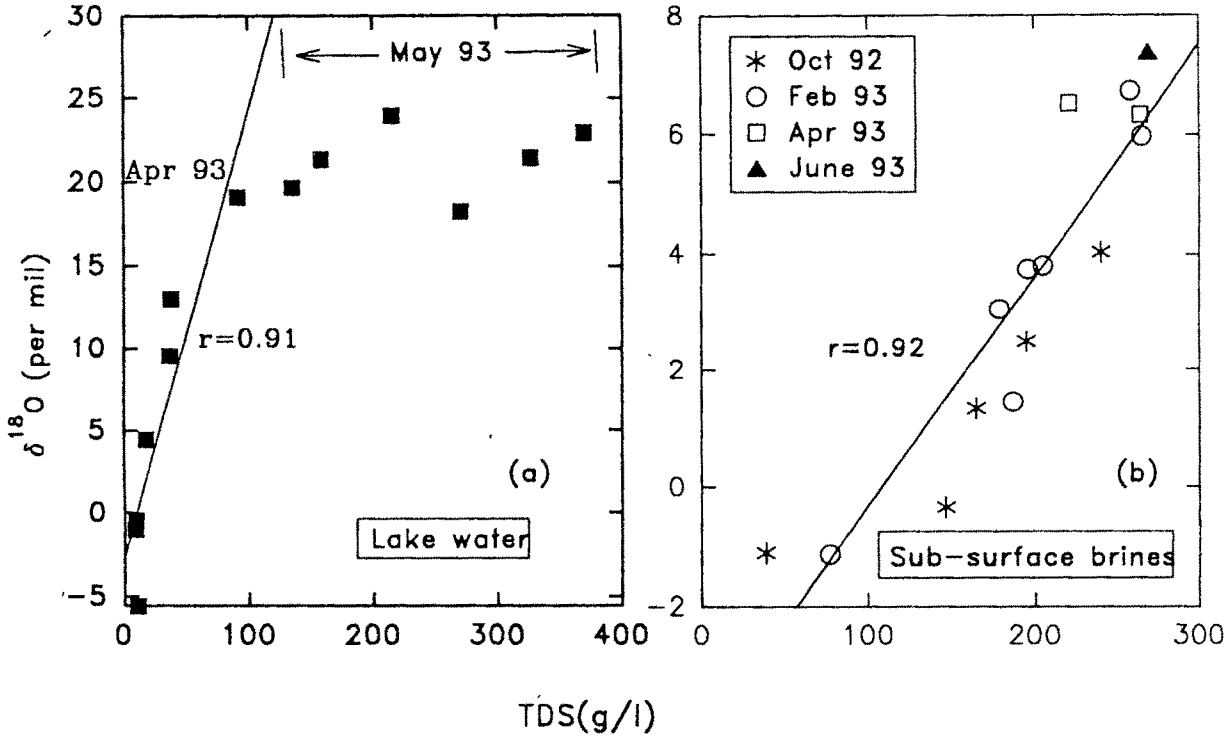


Fig. 7.2 Scatter diagram of oxygen isotopes in lake and sub-surface brines observed during the annual wetting and drying cycles (1992–1993). Fig. 7.2a shows a strong positive correlation (r=0.91) between $\delta^{18}O$ and salt content for the Sambhar lake waters during July 92–Apr 93. Such variation in $\delta^{18}O$ and TDS is explained through the process of evaporation. The $\delta^{18}O$–TDS relationship during late stage of evaporation (May 93) has a much gentler slope, resulting from the back condensation of $\delta^{18}O$ depleted atmospheric water vapour (see text for detail discussion). Fig. 7.2b also illustrates strong positive correlation (r=0.92) between $\delta^{18}O$ and salt content for the sub-surface brines. The linear trend between them is mainly attributed to a two component mixing of waters, i.e. lake/atmospheric precipitation and sub-surface brines.

where δ_0, δ are the $\delta^{18}O$ of initial water and that at any time t respectively, α the oxygen isotope fractionation factor between vapour and liquid and f is the fraction of residual lake water. In this model calculation, the fractionation factor α is considered to be constant throughout the annual evaporation period and δ of each succeeding step was calculated from the preceding δ value [eqn. (7.2)]. The residual fraction of lake water used in model calculation is estimated from concentration of uranium in the water at each evaporation step, as U is known to be a conservative tracer in an oxidising environment (see section 7.3 for detail discussion). The Rayleigh model agrees well with the measured values of $\delta^{18}O$ (assuming $\alpha = 1.0092$) in successive evaporation stages until the residual fraction of water in the lake approaches to around 10% during Apr 93 (Fig. 7.3). In later stages, model derived $\delta^{18}O$ increases sharply and does not fit the experimental data. The divergence in the $\delta^{18}O$ values calculated based on the model and those measured in later stage of evaporation could be attributed to either reduction in equilibrium fractionation factor, reduction in vapour pressure of lake water or by an increased exchange of isotopically light atmospheric water vapour.

To understand the relative importance of these factors, data were analyzed using the Craig-Gordon model where both equilibrium and kinetic fractionation factors, and the effect of changing seasonal temperature and humidity were taken into account.

The evolution of oxygen isotope as a function of time is calculated from the following relations (Gonfiantini,1986):

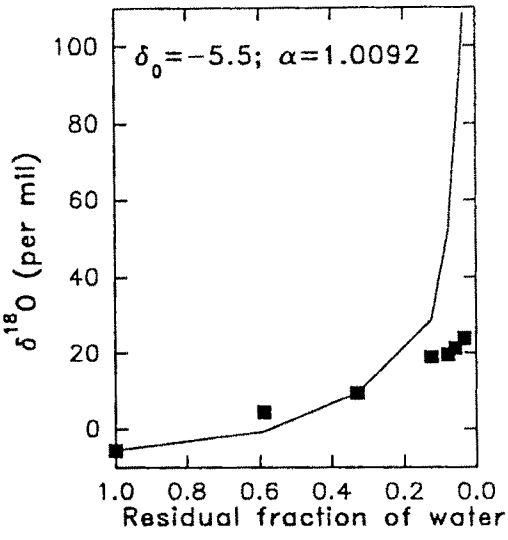
$$\delta = \delta_0 + \frac{d\delta}{d\ln f} \cdot \Delta \ln f \tag{7.3}$$

where,

$$\begin{aligned}
\frac{d\delta}{d\ln f} &= \frac{\frac{h}{a_\omega}(\delta - \delta_a) - (\delta + 1)(\Delta\epsilon + \frac{\alpha - 1}{\alpha})}{1 - \frac{h}{a_\omega} + \Delta\epsilon} \\
\alpha &= \exp(1137/T^2 - 0.4156/T - 0.00207) \qquad (Majoube, 1971) \\
a_\omega &= -0.000543/f^2 - 0.018521/f + 0.99931 \\
\Delta\epsilon &= 0.0142(1 - \frac{h}{a_\omega})
\end{aligned}$$

δ_a is the $\delta^{18}O$ of atmospheric water vapour, h is the fractional relative humidity, T is the temperature in ^0K and a_w is the thermodynamic activity of water.

Fig. 7.3 The annual oxygen isotopic evolution (July 92–May 93) in the Sambhar lake based on Rayleigh fractionation model. The model curve approximates the observed data points up to ~ 10 % of residal lake water. beyond which model curve diverges from observation. See text for explanation in discrepancy of the observed and modelled $\delta^{18}O$ results.



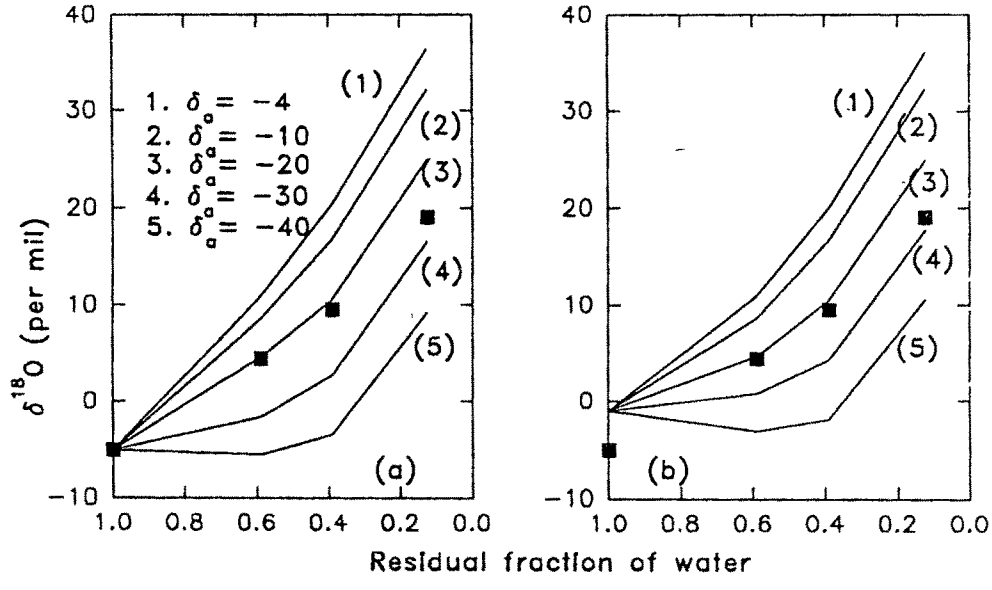


Fig. 7.4 Craig–Gordon (1965) model applied to annual isotopic evolution of oxygen (July 92–May 93) in Sambhar lake waters with initial $\delta^{18}O$ (a) −5.5 and (b) −1 per mil and different isotopic composition for atmospheric water vapour (δ_a). Comparison of Figs. (a) and (b) indicates that $\delta^{18}O$ evolution trend does not depend critically on the initial value. The model curve (3) approximates the observed data for δ_a=−20 per mil.

The Craig-Gordon model calculation was carried out until the residual fraction of lake water was 10%. Further calculations could not be made as the expression for thermodynamic activity of NaCl solution (a_w) is valid only upto the residual fraction f=0.1 (Gonfiantini,1986). The evolution of $\delta^{18}O$ as a function of residual amount of water in the lake was calculated for (i) different values of $\delta^{18}O$ in the atmospheric water vapour (Fig. 7.4) undergoing exchange with lake water and (ii) different initial values for $\delta^{18}O$ in the lake water. These results are presented in Fig. 7.4 which show that (i) the most sensitive variable affecting the $\delta^{18}O$ evolution of lake water is the isotopic composition of the atmospheric water vapour and (ii) the $\delta^{18}O$ evolution in the lake with evaporation is not critically dependent on the initial isotopic composition of either -5.5 or -1.0 $^{o}/_{oo}$. Reasonably good fit with the experimental data (Fig. 7.4) is obtained for the value of -20 $^{o}/_{oo}$ for the atmospheric water vapour. These results suggest that back condensation of isotopically light atmospheric vapour having $\delta^{18}O$ as low as -20 $^{o}/_{oo}$ plays a dominant role on the isotopic evolution of the lake water during the late stage of evaporation. A similar observation has been reported for the Owens lake, California (Phillips et al,1986). The $\delta^{18}O$ of atmospheric water vapour over the Sambhar lake has not been measured. However, a value (-20 $^{o}/_{oo}$) is reasonable for the pre and post monsoon seasons when the western disturbance brings precipitation to regions north of the Sambhar lake. Measurement of $\delta^{18}O$ in atmospheric water vapour of this region is required to confirm the model calculations.

The $\delta^{18}O$ measurements were made in two types of pan waters: different pans with varying salinity collected in a single season (Feb 92) and the same pan sampled at different times during Feb–May 92. The objective behind this study was to understand the relationship between salt content (TDS) and $\delta^{18}O$ of evaporating waters in the pans and to compare the oxygen isotopic evolution in the pan and lake waters during evaporation.

The pan waters collected during a single season (Feb 92) did not prove to be useful for studies as they were a mixture of various end members. It was learnt that water from subsurface brines were periodically mixed with the pan waters and circulated from one pan to the other during salt production. This is unlike the sample from the same pan, which was recharged with lake water only once and allowed to evaporate. The $\delta^{18}O$ evolution of this pan water, therefore, can be compared with the $\delta^{18}O$ evolution in lake waters.

In this comparative study, an assumption is made that the conditions of evaporation have remained the same over the two year periods (91−92 and 92−93) for both lake and pan waters. Fig. 7.5 shows the variation in $\delta^{18}O$ as a function of salt content. The $\delta^{18}O$ evolution shows a positive relation with TDS and does not saturate, unlike the lake waters. Also, the maximum $\delta^{18}O$ (27.5 $^{o}/_{oo}$) observed in the pan is relatively higher than that observed in lake waters (mean value, 21$^{o}/_{oo}$). Such an observation indicates difference in evolution pattern of $\delta^{18}O$ in pan compared to that of the lake. This could arise due to the high rate of evaporation in the pan for less volume of water spread over large area. Under such a condition, the process of evaporation dominates over the back condensation of atmospheric water vapour which is depleted in $\delta^{18}O$.

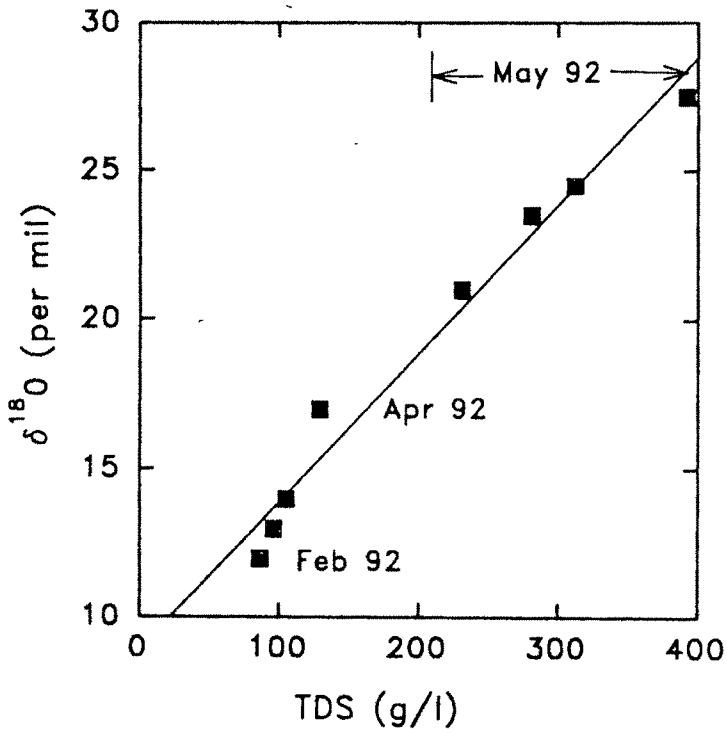


Figure 7.5: Scatter diagram of salt content (TDS) and oxygen isotope ($\delta^{18}O$) in an evaporating pan sampled during different months (Feb−May 92). The samples collected include hyper saline brines up to a stage of halite precipitation. The $\delta^{18}O$ evolution pattern in pan is different from the lake waters, see Fig. 7.2a

In contrast to the evaporating lake waters, the seasonal variations in the $\delta^{18}O$ are less pronounced in sub-surface brines. The temporal evolution of $\delta^{18}O$ in sub-surface brines has been explained in earlier studies through evaporation pattern of a "terminal lake" in

which evaporation is more or less balanced by inputs from precipitation and surface run-off during monsoon season (Ramesh et al,1993). Using a Rayleigh isotopic fractionation model for the typical temperature and humidity conditions (temp. 291^{0}K, humidity 55%) found in this region, they have shown that the saturation in $\delta^{18}O$ is about 4.8 $^o/_{oo}$ which is quite similar to that observed in most of the samples measured in this study during seasons other than the monsoon. With the onset of monsoon (July–Sept), the lake and the open dug wells are recharged by the meteoric water. As mentioned earlier, a number of open dug wells have been constructed on the lake bed for pumping out the sub-surface brines for salt production. These open wells get filled with rain water during monsoon and thus promotes recharge of sub-surface aquifers with atmospheric precipitation. However, the mixing of meteoric water with higher density sub-surface brines may be constrained, the pumping operations carried out for salt production after monsoon season may aid this mixing process. In the sub-surface brines, the mean $\delta^{18}O$ for the month of Oct 92 was lowest ($1^o/_{oo}$) and by June the value increased to 7 $^o/_{oo}$ (based on sample from one of the wells). The $\delta^{18}O$ in sub-surface brines sampled between Oct 92 to June 93 show a significant positive correlation (r=0.92) with the salt content (Fig. 7.2b). Such linear trend for sub-surface brines could be due to mixing with meteoric and/or lake waters during monsoon season and with lake waters during post monsoon seasons. The range in $\delta^{18}O$, -1 to 4 $^o/_{oo}$, of different wells in a single month (Oct 92), shows that the extent of dilution of sub-surface brines with relatively depleted $\delta^{18}O$ end-member (direct precipitation or lake water) is not uniform. A factor contributing to the different extents of mixing of two water bodies (rain or lake water and sub-surface brines) is the variable draw down of the sub-surface aquifer by pumping during salt production. In above consideration, the influence of evaporation on controlling the salinity of sub-surface brines has not been taken into account as these brines occur below the lake bed where evaporation would be resrticted and the $\delta^{18}O$ evolution trend would be unlike of the evaporating lake water.

Synthesis

The $\delta^{18}O$ of shallow groundwaters and riverwaters adjacent to the lake are similar to those in atmospheric precipitation indicating that these water bodies are recharged from

local precipitation. The $\delta^{18}O$ results for the lake and sub-surface brines suggest that these reservoirs are recharged during the monsoon season. In lake, the $\delta^{18}O$ during monsoon is very similar to that of local rain waters, whereas in sub-surface brines $\delta^{18}O$ is enriched, reaches a minimum value of $-1\ ^{o}/_{oo}$ compared to a value of $-5.5^{o}/_{oo}$. The similarity in the $\delta^{18}O$ and of the lake and rain water indicates that the lake gets recharged from atmospheric precipitation and surface run-off. The recharge to sub-surfacae brines from evaporating lake waters during the summer months (Apr–June) is limited as reflected from the large difference in $\delta^{18}O$ measured in the two reservoirs. The lake waters undergo intense evaporation showing $\delta^{18}O$ values as high as $\sim 21^{o}/_{oo}$ during the peak summer (May). In contrast, the sub-surface brines show enrichment in $\delta^{18}O$ only up to $7^{o}/_{oo}$. The $\delta^{18}O$ evolution trend in Sambhar lake is essentially of Rayleigh type, however, the exact trend can be explained through the Craig-Gordon (1965) model. The results of the Craig-Gordon model suggest that back condensation of atmospheric moisture ($\delta^{18}O \sim -20^{o}/_{oo}$) during late stage of evaporation controls the observed $\delta^{18}O$ of the lake brines. A distinct difference in $\delta^{18}O$ evolution trends between the lake and evaporating pan has been observed. The evaporation dominates over the back condensation of atmospheric water vapour even during the late stage of evaporation. Such conclusion is borne out from the linear relation between the $\delta^{18}O$ and TDS in the evaporating pan waters all through the evaporation.

7.2 Major ion composition

The major ion chemistry of various water bodies in the Sambhar lake basin forms an integral part of this thesis as this has relevance to the source of salt to the lake and evolution of brines during the annual evaporation cycle. In addition, such a study also provides a means to characterize the various water bodies in terms of their chemical composition.

The Na and Cl concentrations in the two rain water samples collected during July 93 correspond to ~ 2 mg/l NaCl (Table 7.1). The Na/Cl ratio in these two samples (0.72 and 1.12, Table 7.1) are on either side of the seawater composition (0.85). As the rain samples were collected from the Sambhar town, within a few km of the lake, part of the NaCl in

the rain could arise from its resuspension during salt production from the lake. Therefore, the content of NaCl in these rain water samples may have a local cyclic salt component, in addition to the marine component. The measured NaCl concentration in the two rain water samples, if typical of rains throughout the year, can provide an estimate of the NaCl supplied to the lake via precipitation. The estimate could be an upper limit as there could be a significant local recycling component of NaCl in rain water. The estimate is about 5000 tonnes based on NaCl concentration of 2 mg/l in the rain water, drainage area of about 5600 km^2 (Bhattacharya et al,1982) and an annual rainfall of 50 cm. This estimate when compared to the current annual salt production of 2×10^5 tons/y, suggests that the rain water is not a major contributor of salt to the lake which can sustain the current annual salt production.

An independent approach to evaluate the significance of the rain water contribution of NaCl is by comparing it with the total salt content of the lake after the monsoon. For lake area of $\sim$225 km^2, water depth of 1 m and 8.3 g/l NaCl salt, the inventory of NaCl in the lake is 18.5×10^5 tons which is many orders of magnitude higher than the atmospheric precipitation.

The river waters from the region are more saline than the rain water, with TDS ranging between 0.5–1.8 g/l (Table 7.1), with Na and Cl being the dominant components. The Na/Cl ratio in the river waters ranges between 1.9 to 3.7 with an average value of 2.7 (Table 7.1). There is an excess of sodium over chloride in these waters, which suggests that a significant part of Na is derived from the sources other than NaCl, such as weathering of silicate rocks along the river drainage basin. The TDS content of all the river water samples analyzed are significantly lower than that of the lake water sampled immediately after the monsoon season (samples: SL-46, SL-47, SL-52; Appendix–B, Table 1B). Also, the Na/Cl ratio in waters from the river basin is significantly higher than that observed in lake waters (1.08 average Na/Cl). The high TDS and the low Na/Cl ratio in the lake water compared to that in rivers results from dissolution of halite salt encrustation from the lake bed during the recharge period. These results seem to indicate that the contribution of salt from inflow river waters to the lake is significantly less compared to that recycled from within the lake basin. The average Na/Cl ratio in river waters is 2.70 (Table 7.1). If 125 meq/l of Na and Cl are added to river waters (see Appendix–B, Table 2B) then

Na/Cl ratio reduces to about the same value of lake waters. Such an addition indicates that the contribution of NaCl to the lake water by recycling of salts in the lake is about 90% and rest can be from the surface run-off. A rough estimate on the amount of NaCl recycling from the lake basin, based on NaCl content in lake water of 1 m average depth during Oct 92, is calculated to be $\sim 18.5\times10^5$ tons.

The TDS content of groundwaters ranges from 0.5 to 12.3 g/l but in most of the samples it centers around ~2.0 g/l with Na and Cl accounting for ~70% of the cations and anions (Table 7.1), suggesting general dominance of NaCl in the drainage basin. The Mg/Ca ratio in some of the groundwaters is > 1. This can arise due to preferential removal of Ca by mineral precipitation from these water bodies. In fact, most of the groundwaters are supersaturated with respect to calcite.

The chemical evolution of lake and pan waters was studied by analyzing samples collected during different seasons. The chemical composition of waters from these two reservoirs during their evaporation cycles is generally similar, consistent with that expected as the lake water is the dominant component of initial end-member used in the evaporating pans. The TDS content in the lake waters ranges from 9 to 370 g/l (Table 7.1), the lowest values occurring in samples collected during the period immediately following the monsoon season (Oct 1992) and highest value during the summer season just before the monsoon.

7.2.1 Chemical evolution of the Sambhar lake brine

Hardie-Eugster model

The evolution of brines in closed sedimentary basins due to evaporation of waters depends on several factors e.g. initial composition of water, mineral precipitation, selective dissolution of salt encrustation, ion exchange and sorption processes, degassing and redox reactions (Eugster and Jones,1979). Major solutes present in source water are affected differentially by these processes. Out of these, mineral precipitation is a dominant process that governs the chemical evolution of brines during evaporation (Garrels and Mackenzie,1967; Hardie and Eugster,1970; Eugster and Hardie,1978; Eugster and Jones,1979). As a consequence of evaporation, the evaporating waters follow a definite brine evolutionary path based on the concept of "Chemical Divide" (Drever,1988). The concept of chemical

divide is generalized by Hardie and Eugster (1970) for several natural water compositions. In most natural waters, calcite($CaCO_3$), is the first mineral to precipitate, followed by either gypsum ($CaSO_4.2H_2O$) or sepiolite (Mg-silicate)(Hardie and Eugster,1970). If Ca is less abundant than alkalinity (abbreviated as Alk), all the Ca would be precipitated as $CaCO_3$ and the brine would become alkaline. On the other hand, if Alk is < Ca, then (HCO_3 + CO_3) would be precipitated out and the brine would be neutral along the Cl–SO_4 path (Drever,1988). Such a brine evolution path is valid for precipitation of calcite only, however, for a combination of minerals such as calcite and sepiolite the brine evolutionary path is determined by the ratio of Alk/(Ca + Mg).

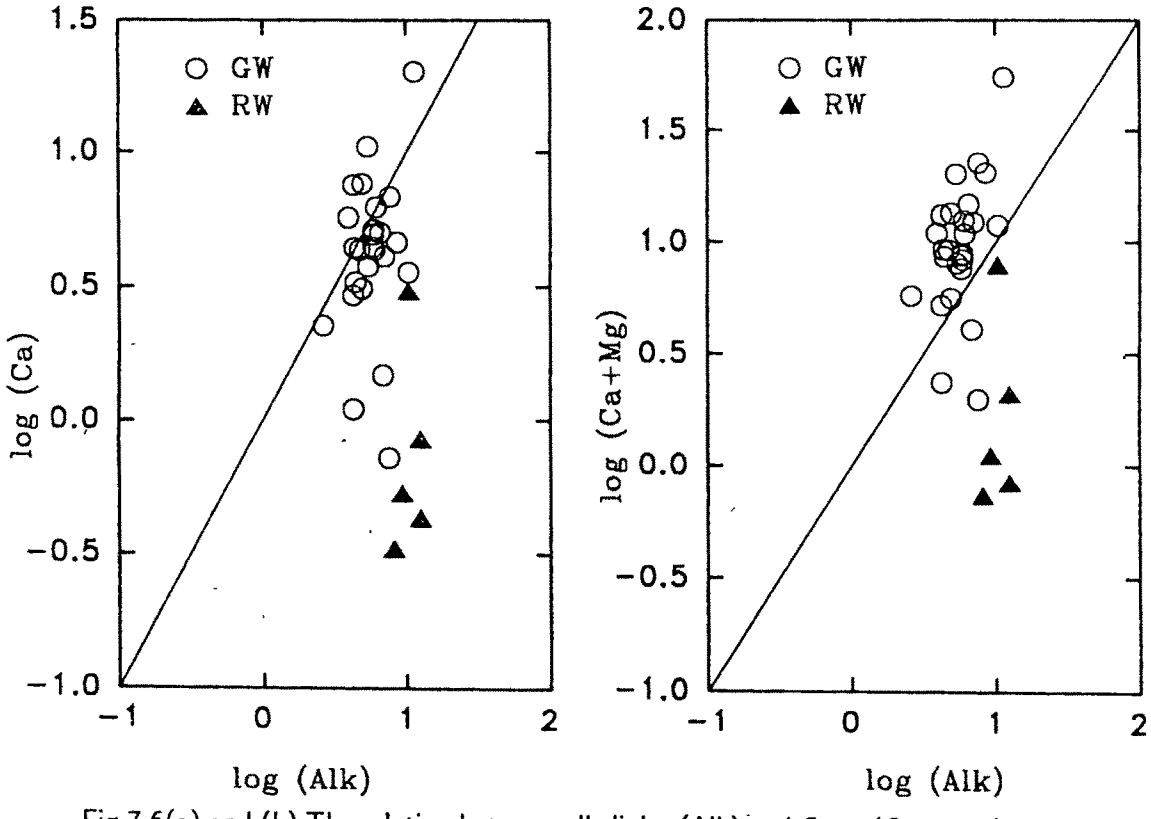


Fig.7.6(a) and (b) The relation between alkalinity (Alk) and Ca or (Ca + Mg) concentrations in ground and river waters of the Sambhar lake region. All the river waters and a few groundwater samples have Alk more than that of either Ca or sum of Ca and Mg. The evaporation of these waters would result in alkaline brines. Those having Alk less than the sum of Ca and Mg ions would produce neutral brines on evaporation (Hardie and Eugster,1970; Eugster and Hardie,1978; Eugster,1980; Drever,1988).

The effect of precipitation of sepiolite, smectite and dolomite on the alkalinity of the

brines is similar (Drever,1988); for this reason in model calculations later presents only one of the Mg-minerals such as sepiolite which is within the scope of the Hardie-Eugster model. Figs. 7.6a and 7.6b show the relation between Ca and (Ca+Mg) with Alk in groundwaters and river waters in and around the Sambhar lake. The data show that in most groundwaters alkalinity is greater than Ca concentration but it is less than the sum of the concentrations of Ca and Mg. On the other hand, all river waters have Alk greater than either Ca or sum of the concentrations of Ca and Mg. As stated earlier, following the principle of "chemical divide" evaporation of groundwaters would result in a neutral brine whereas alkaline brine would be produced by river waters if calcite and sepiolite both precipitate. As silica concentration was not measured in these waters it is assumed that the various source waters have silica concentration equal to that of amorphous silica activity (i.e. $10^{-2.7}$).

The evolution of the Sambhar lake brine has been studied following the Hardie-Eugster model (1970) (cited hereafter as H-E model). The various conditions imposed in the model calculation according to the H-E model are that the water remains in equilibrium with a CO_2 partial pressure of $10^{-3.5}$ atm., temperature remains constant at 25^0C, and pure water is continuously removed from the system. It has been further assumed that there is no interaction between solid formed and residual water during the evaporation. Also, the model calculation neglects the "ion-pairing" effects. The simulation study of evaporation was performed by increasing the concentrations of various ion species in small steps and keeping a constant track on pH, I (ionic strength), m (molality) and γ (activity coefficient) for the various pH dependent species (Hardie and Eugster,1970). The model calculation was terminated at ionic strength of 5, as beyond this ionic strength the Debye-Huckel relation used for calculating the activity coefficient of individual ion is questionable. Even for samples having ionic strength >1, the activity coefficient of ions based on Debye-Huckel relation diverges from experimental results (Garrels and Christ,1965), however, the overall evolution trend of brine can still be ascertained through the H-E model. The programming and other details of the model calculation were checked using the data from the Sierra Nevada spring water, the evaporation trend for which are reported (Garrels and Mackenzie,1967). The results show that the overall evolution trend with regard to pH, concentrations of Ca, Mg, Na, Cl, HCO_3, CO_3 and SO_4 species are similar between

those published in literature and that calculated in this study (Fig. 7.7); though there is some minor discrepancy related to the precipitation stage of calcite. This discrepancy results from different value of γ used for the Ca.

Table 7.2: Chemical composition† of source waters used for modelling the evolution of Sambhar lake brines following the Hardie–Eugster model (1970)

Reservoir	pH	Na	K	Ca	Mg	Cl	SO_4	Alk
R. Roopangarh	8.0	14.6	0.32	0.215	0.233	4.65	0.633	9.9
R. Mendha	8.2	24.1	0.365	0.972	1.525	9.75	4.15	11.35
Groundwaters	7.94	21.5	0.09	1.65	2.67	24.33	0.75	4.4
Lake water	8.4	142.6	0.31	0.665	0.185	129.28	4.165	7

† concentrations are expressed in mmol/l and charge balance of the solution is adjusted with respect to the chloride ion.

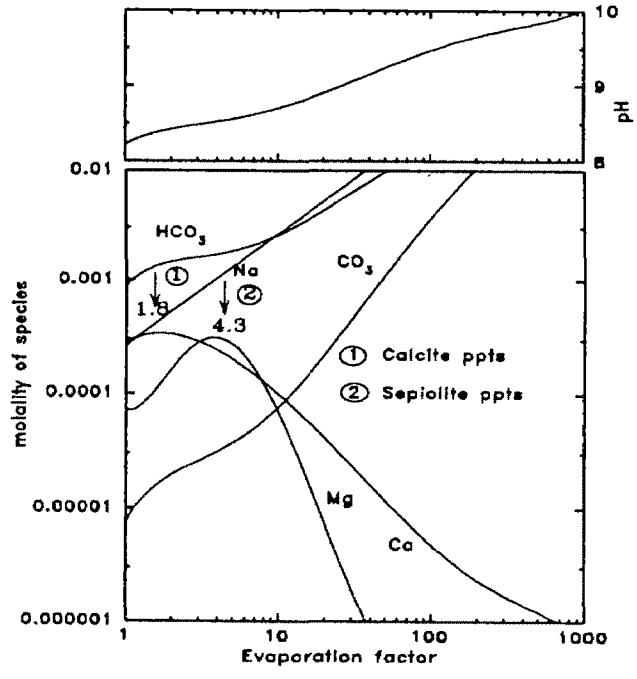


Figure 7.7: Calculated results of evaporation of Sierra Nevada spring water at constant temperature (25°C) in equilibrium with atmospheric P_{CO_2}. The chemical evolution during evaporation essentially follows the trend published by Garrels and Mackenzie (1967). This calculation was carried out to test the details of programming the H-E model.

The evolution of the Sambhar lake brine was simulated using several initial endmember water compositions e.g. the average composition of the two river waters, lake water collected just after the monsoon period and a typical groundwater (Table 7.2). The

charge balance in analytical data was achieved through Cl adjustment. The evolutionary trend obtained by evaporating the Sambhar lake water collected during Oct 92 agrees well with the experimental data in terms of increasing concentrations of Na, K, Alk and SO_4. Some of these results are shown in Fig. 7.8. The pH data for different stages of evaporation are not available to check the model results, however, the pH measurement made in one of the pan brines (SL-7, Appendix–B, Table 2B), of which the lake waters constitute a major component, showed value of about 9.5 at I=5.5. Such a value of pH agrees with the model predicted result for the lake brine (Table 7.3). A major discrepancy has been observed in the evolutionary trend for Ca and Mg ions at different stages of evaporation. The measured concentrations of Ca and Mg ions are much higher than the model predicted values (Fig. 7.8). The possible explanations could be "ion-pairing" and complex ion formation which are ignored in the model calculation. The other possibility, though very unlikely, could be the overestimation of the concentrations of Ca and Mg during measurement as the analysis was done directly in the brine.

Table 7.3 Model calculated* chemical composition of the brine

Chemical composition of brine at Ionic strength,I=5										
Reservoir	pH	Na	Ca	Mg	Alk	SO_4	Cl	Na/Cl	Na/Alk	Cl/SO_4
Lake water (1)	9.8	4.79	1.2×10^{-6}	0	0.19	0.32	4.52	1.06	25	14
Lake water (2)	-	5.0	1.0×10^{-4}	1.5×10^{-4}	0.20	0.40	4.44	1.13	25	11
R. R	10.4	3.82	0	0	2.36	0.32	1.21	3.16	1.6	3.8
R. M	10.2	3.87	2×10^{-7}	0	1.0	1.34	1.57	2.46	3.8	1.2
Groundwater	6.9	3.81	0.76	3.5×10^{-4}	1.3×10^{-4}	0.26	4.31	0.88	3×10^{4}	16.6
R.R. + salt	9.9	4.97	6×10^{-7}	0	0.32	0.044	4.62	1.08	15.5	105
R.M. + salt	9.8	4.45	2.5×10^{-7}	0	0.22	0.24	3.31	1.34	20	14

* ion concentrations in eqv./l and ion ratios in eqv.
Lake water(1) is model calculated and Lake water(2) is the observed value at I =5.2 for SL-77
R.R.and R.M. indicate the river Roopangarh and Mendha respectively.
- indicates measurement not made

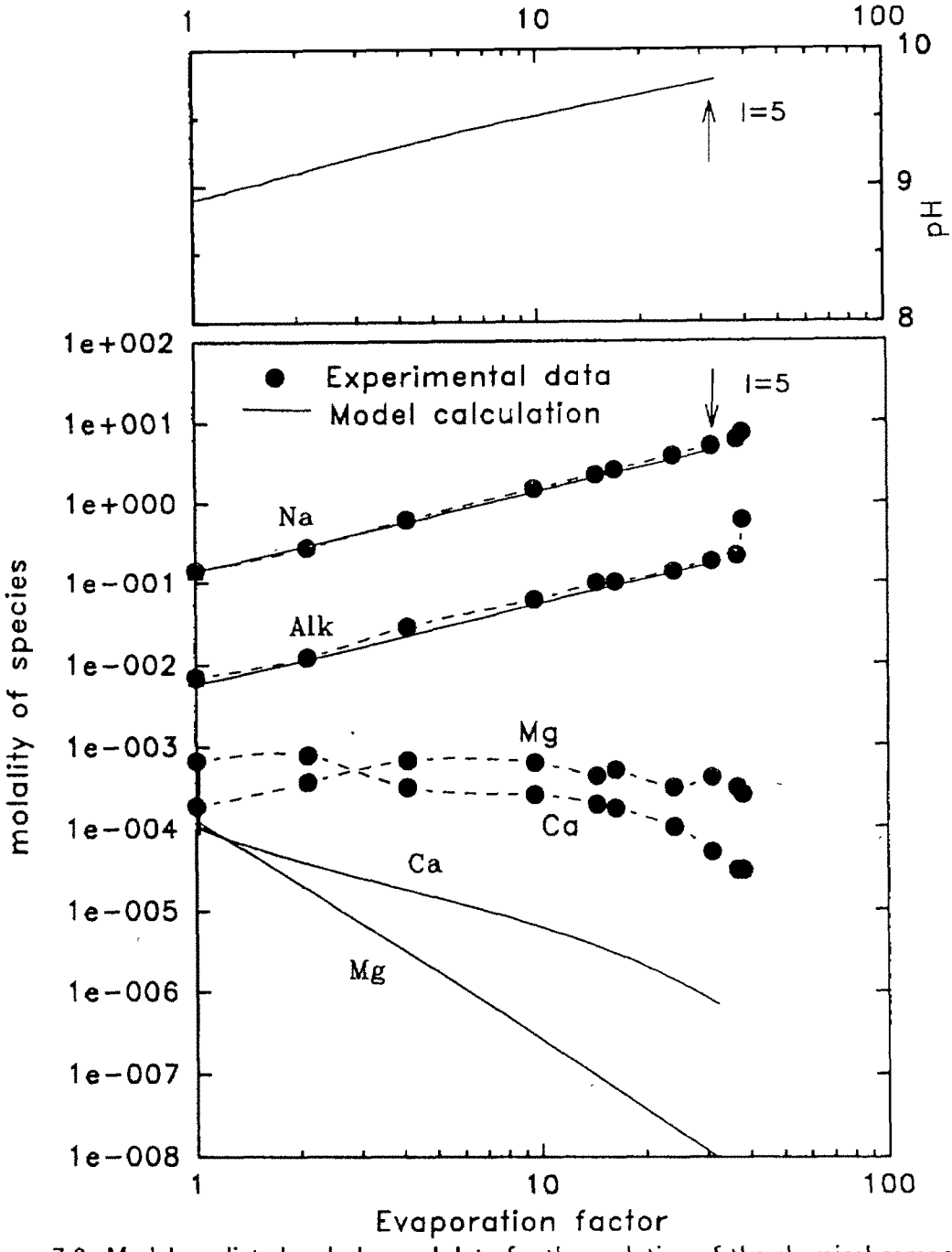


Figure 7.8: Model predicted and observed data for the evolution of the chemical composition of the Sambhar lake waters during annual evaporation. The source water used in the model calculation is the sample SL-46 collected from the lake during Oct 92 . The model calculation was terminated at ionic strength, I=5.

The model calculations were repeated using the two river waters (R. Roopangarh and R. Mendha abbreviated by R.R. and R.M.) as the initial endmembers. These waters have an average TDS value of about 1.2 g/l, significantly lower than that of the lake water endmember. Because of this low TDS, the river waters had to be evaporated much more than that was done earlier using the lake water as the initial endmember to obtain ionic strength of 5. As expected, based on the initial ratio of Alk/(Ca+Mg) greater than one, these river waters produced alkaline brine which is essentially devoid of Ca and Mg ions. The Ca and Mg concentrations decreased during successive stages of evaporation due to their removal as calcite and sepiolite minerals. The other ions such as Na, Cl, SO_4 and Alk showed a linear increase in their concentrations due to evaporative enrichment (Figs. 7.9a and 7.9b). The pH of the brine is ~10 slightly more alkaline than that measured in ione of the pan brines (sample SL-7, pH~9.5, Appendix–B, Table 2B) at I=5.5. Though the trend of the evolution of many of the major ions in Figs. 7.9a and 7.9b is similar to that of the Sambhar lake, the ratio of various ions in the brine, calculated based on the model, and those observed in the lake are distinctly different (Table 7.3).

For example, the Na/Alk and Cl/SO_4 measured in the brine is ~ 25 and ~ 11, compared to the calculated values of 1.6 and 3.8, respectively in R.R. based on the H-E model (Table 7.3). The calculated Na/Cl ratio is also quite different from the observed result. Similar results were obtained when the calculation was repeated for the river Mendha water as the initial endmember (Table 7.3). Based on these ratios, it seems that evaporation of pure R.R. and R.M. endmembers cannot produce the chemical composition of the brine observed in the Sambhar lake. Such a discrepancy can be explained in terms of the chemical composition of the endmembers. The lake water is mainly of Na–Cl type whereas in river waters Na, Cl and HCO_3 constitute the dominant components of the total dissolved salts. One approach to obtain better agreement between the calculated and observed chemical composition is to enrich the initial endmember with NaCl, a process which is very likely to occur during the wetting cycle of the lake when halite crust from the lake bed could dissolve. As a test case, Na and Cl contents were increased in the R.R. and R.M. waters by 125 and 120 mmol/l respectively to match the Na and Cl content of lake water initial endmember.

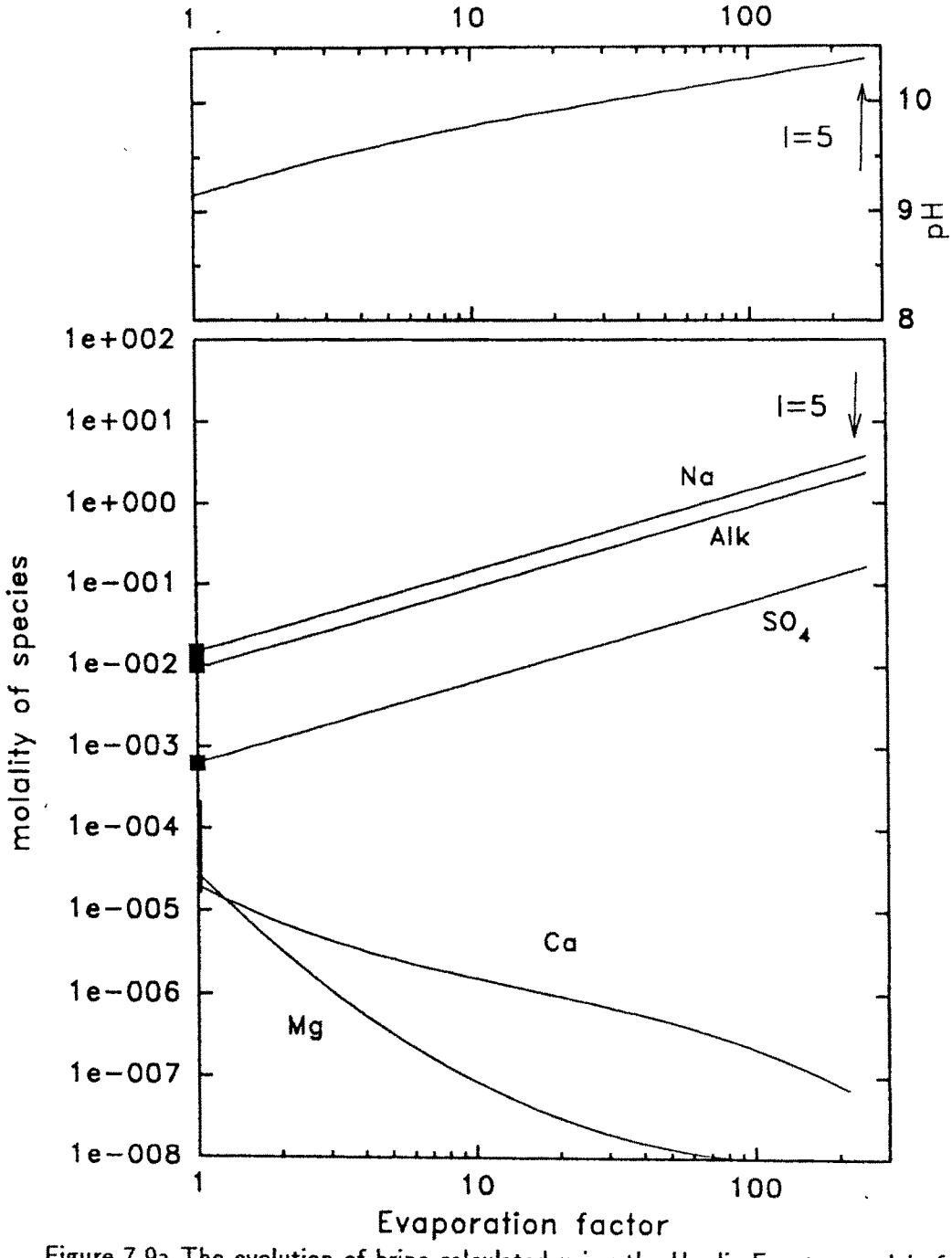


Figure 7.9a The evolution of brine calculated using the Hardie-Eugster model of evaporation for the Roopangarh river water as the initial endmember. The evolution trends of pH, Na, Ca, Mg, Alk and SO_4 is found to be similar with the Sambhar lake water (Fig. 7.8), however, the ion ratios in the calculated brine differ from the lake waters. The model calculation was terminated at ionic strength,I=5.

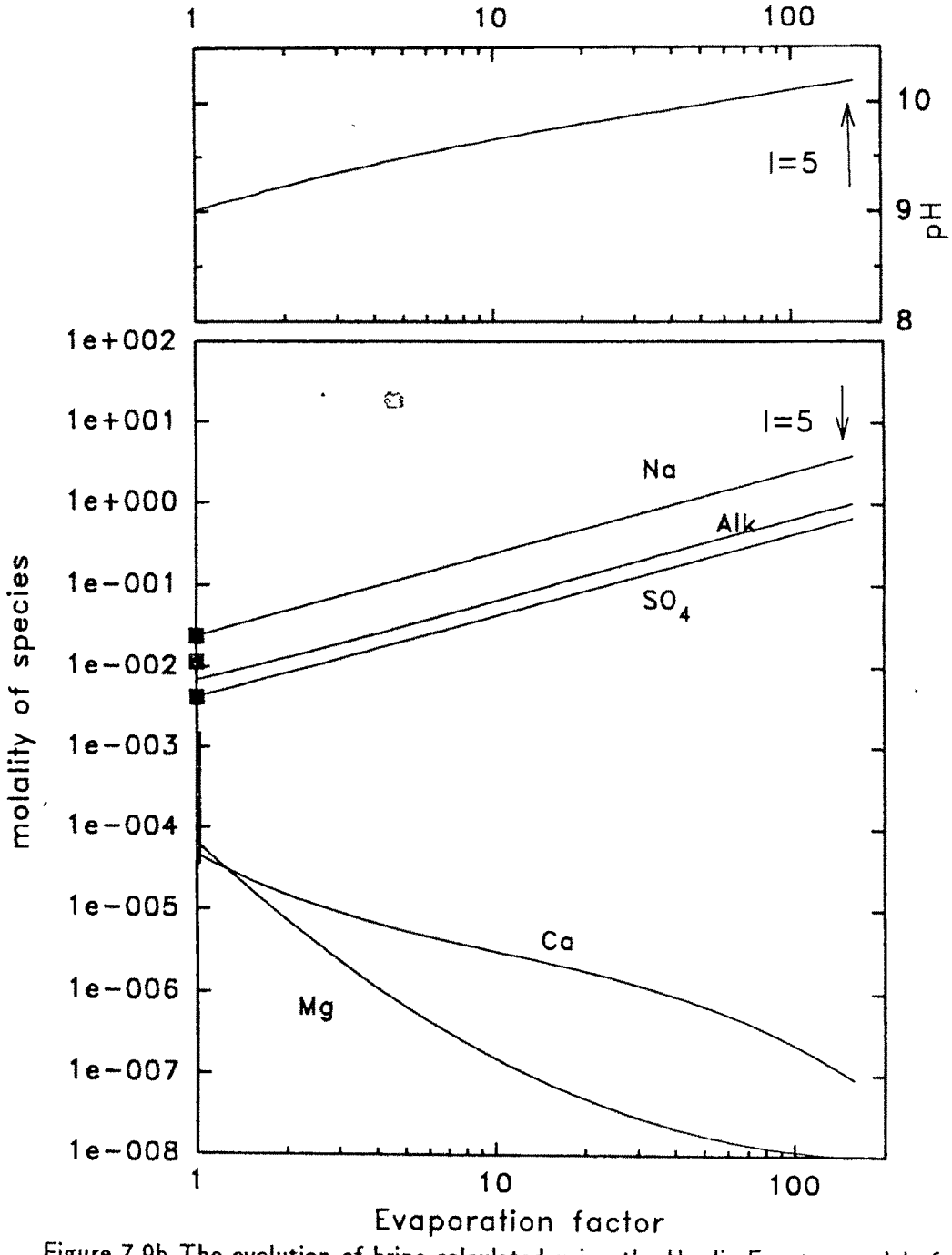


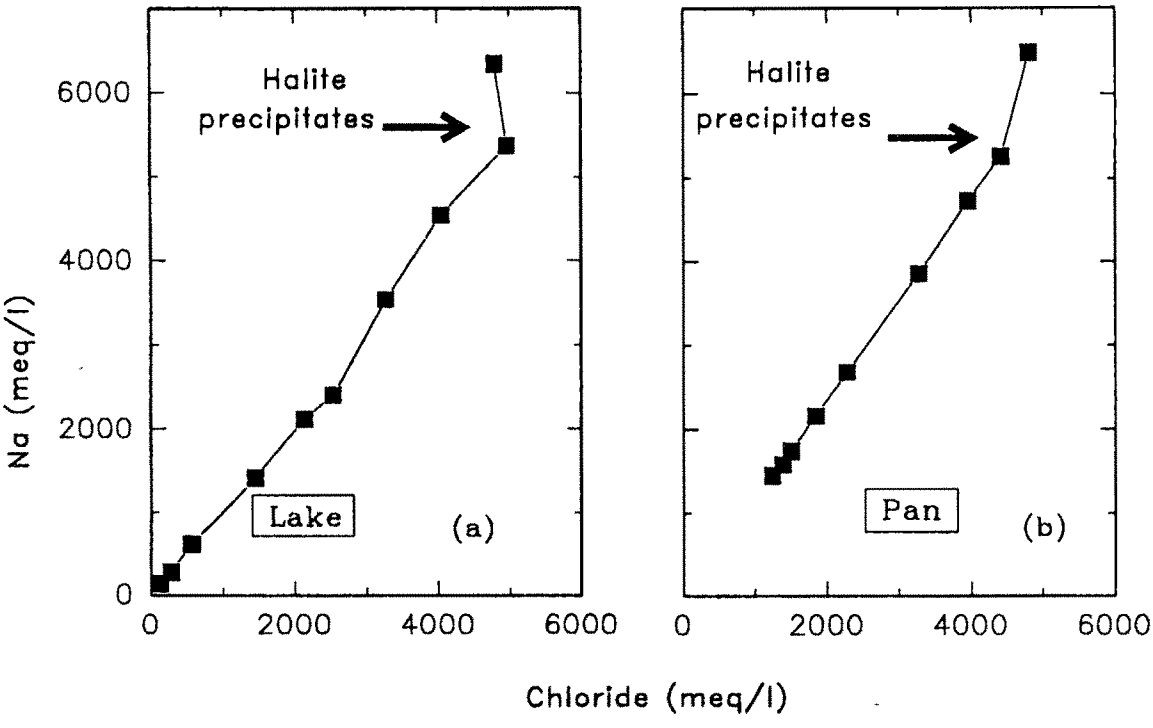
Figure 7.9b The evolution of brine calculated using the Hardie-Eugster model of evaporation for the Mendha river water as the initial endmember. The evolution trends of pH, Na, Ca, Mg, Alk and SO_4 is found to be similar with the Sambhar lake water (Fig. 7.8), however, the ion ratios in the calculated brine differ from the lake waters. The model calculation was terminated at ionic strength,I=5.

Evaporation of these modified river waters resulted in Na-Cl type and alkaline brines (pH of the brine at I=5 found to be 9.9 and 9.8 respectively for R.R. and R.M. waters). The ratios of Na/Alk and Cl/SO_4 in the brines at I=5 are 15.5 and 105 for R.R. and 20 and 14 for R.M. waters. These values are in better agreement with the measured values of the Sambhar lake brine compared to those obtained by evaporating pure R.R. and R.M. waters as the initial endmembers.

The H-E model calculation using a typical groundwater as initial endmember was also done to follow its chemical evolution during evaporation and compare the results with the lake brine. The groundwater chosen for this purpose has Alk/(Ca+Mg) ratio < 1, typical of most of the groundwaters adjacent to the lake (Fig.7.6b). As expected, the calculated brine composition is Na-Cl type but neutral (pH $\sim$7) in character. Based on this result, it appears that evaporation of such groundwaters cannot account for the type of brine available in the lake basin. However, mixing of river and groundwaters (e.g. 80% R.R. + 20% groundwater, Table 7.2) can produce a resultant water with Alk/(Ca + Mg) >1, which can produce an alkaline brine on evaporation. Such a brine also differs from the observed lake brine in terms of Na/Cl, Na/Alk and Cl/SO_4 ratios.

The above calculations, therefore, suggest that it is difficult to account for the observed chemical composition and ion ratios by evaporating pure initial river and groundwater endmembers for the region. Important processes governing the Sambhar lake brine evolution is the recycling of salt during the recharge period from the salt encrustation in the lake bed followed by the mineral precipitation such as the calcite and sepiolite or dolomite during evaporation. The recycling of salt from lake basin during recharge period is also evidenced from the low Na/Cl ratio (as discussed earlier) and low U/TDS ratio which will be discussed in the next section.

Another approach to identify the freshwater endmember for evolution of Sambhar lake brine can be made by studying the behaviour of major solutes (i.e Na and Cl) after halite saturation. The major ion Na shows a significant increase in its concentration with respect to the Cl both in lake and pan waters after halite saturation (Figs. 7.10a and 7.10b). Such an increase in Na over Cl provides a clue to the brines parent water composition with Na/Cl ratio > 1 based on the concept of "Chemical divide" (Drever, 1988).



Figures 7.10a and 7.10b: Variation in the abundances of Na as a function of chloride during evaporation of the lake and pan waters, a major change in trend is seen beyond halite crystallization stage.

According to the chemical divide concept, Na concentration should increase relatively with respect to chloride after halite saturation for the initial water composition having Na/Cl ratio >1. In fact, Na concentration should increase followed by a decrease in Cl concentration after the the halite crystallization so that ion activity product of NaCl remains constant. Such an indication is seen only with the lake waters (Fig. 7.10a). In pan waters, decrease in Cl concentration after halite saturation is not observed which could be due to limited data. In order to observe the above trend, more number of samples are required to be analyzed after the halite crystallization. It was observed that the lake waters immediately after monsoon season had an average Na/Cl ratio of 1.08 (Table 7.1). Considering average Na/Cl ratio in all freshwater endmembers, it is found that only river waters do have Na/Cl ratio >1 and groundwaters have this ratio $\sim$ 1 (Table 7.1). Therefore, groundwaters alone cannot be considered as the initial endmember for the evolution of Sambhar lake brine. With these results, it is apparent that a multiple

component of waters viz. river waters, groundwaters and rainwaters can be considered for the Sambhar lake brine evolution.

The TDS content of the sub-surface brines over an annual evaporation cycle ranges between 40−270 g/l (Table 7.1). A range of TDS, 40 to 240 g/l, observed in sub-surface brines during Oct 92 (soon after monsoon) could be attributed to non-uniform mixing of meteoric waters. This observation is consistent with the $\delta^{18}O$ results observed during the same season. Similar to lake waters, both Na and Cl are the major ions, accounts for nearly 90% of the TDS and average Na/Cl ratio is 1.2 (Table 7.1). Among the sub-surface brines a striking difference in Alk and (Ca,Mg) concentrations has been observed in few samples collected from Khakarki along the periphery of lake. The Alk in these samples is lower and (Ca,Mg) concentrations are higher by about one and three orders of magnitude respectively compared to that from the lake bed. In addition to the major ion differences, the $\delta^{18}O$ is also unusually -1.12 and $1.45\ ^{o}/_{oo}$ in these two samples which were collected during winter season (Feb 93). The relatively depleted $\delta^{18}O$ in these samples reflect possibly influence of mixing of the adjacent groundwaters with the sub-surface brines. The above results, therefore, indicate that some of the sub-surface brines are chemically and isotopically different from those mainly available at salt producing sites.

7.2.2 Aqueous mineral equilibria

As discussed earlier, mineral precipitation in evaporating waters governs the brines evolutionary path. The identification of authigenic minerals in solid phase such as the lake's sediment would provide information about the minerals controlling the brines evolution. However, among the Mg-minerals e.g. dolomite, smectite and sepiolite all have similar effects on alkalinity of the evolving brine from evaporation of freshwater endmember (Drever,1988). The minerals precipitating from waters to solid phase can be judged from their positive saturation indices (SI) in waters and their actual presence in the solid phase. The calculation of SI for the common minerals and their identification in solid phase such as the sediments and bitteren crust have been made in this study, as mentioned below.

The saturation state of various minerals present in all water types analyzed in this study is calculated based on ion activity product of the individual ions. In this context, the SI of the mineral is defined by log(IAP/K), where IAP is the ion activity product

and K is the equilibrium constant of the mineral concerned. The Debye–Huckel relation was used for all freshwater samples (river waters and groundwaters) and a computer program PHRQPITZ (Plummer et al,1988) especially designed for brines calculation was used for all saline water samples (TDS > 70 g/l). The PHRQPITZ has incorporated thermodynamic data base of Harvie and Weare (1980) and Harvie et al (1984), and takes care of the effects of ion pairing and complex ion formations. All the water types viz. river waters, groundwaters, lake waters and sub-surface brines are found to be supersaturated with respect to calcite and dolomite minerals but undersaturated with gypsum (Table 7.4).

Table 7.4 Saturation index (SI) of a few common minerals in various water reservoirs in and around the Sambhar lake

Water type	SI(Calcite)	SI(dolomite)	SI(gypsum)
River water	**0.89–1.89**	**2.29–4.39**	**-(3.33–1.69)**
Groundwater	**0.74–2.29**	**1.94–6.82**	**-(2.77–0.86)**
Lake water	**0.54–1.04**	**0.70–2.73**	**-(3.47–2.05)**
Sub-surface brine	**0.02–1.04**	**0.70–2.73**	**-(3.47–2.05)**

X-ray diffraction (XRD) analysis was done on the sediment sample from the lake bed and the bittern crust to substantiate some of the minerals crystallizing from evaporating lake water. The XRD results for sediments confirm the presence of calcite and dolomite minerals, however, there is no indication of these minerals in bittern crust. Such an observation indicates that Ca-Mg minerals are precipitated out from the lake waters during early stage of evaporation and hence they cannot be identified in the last stage of brine i.e. the bittern crust. The bittern crust sample showed the presence of carbonate and sulphate minerals besides halite such as trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), thenardite ($Na_2SO_4$) and burkeite ($2\ Na_2SO_4 \cdot Na_2CO_3$). Except halite none of these minerals have been found to be saturated in the brine (Table 7.5). It could be possible that these minerals precipitate from the brines during much later evaporation stage. A conclusion can be made based on aqueous mineral equilibria that since all water bodies in and around the Sambhar lake are supersaturated with respect to calcite and dolomite minerals, it implies essentially similar

weathering environment.

Table: 7.5 Saturation states of minerals in a Sambhar lake brine sample

SL-3 pH=9.48 Ion strength= 7.66	
	SI†
Aragonite ($CaCO_3$)	0.35
Burkeite ($2\ Na_2\ SO_4 \cdot Na_2CO_3$)	−0.84
Calcite ($CaCO_3$)	0.54
Dolomite ($CaCO_3 \cdot MgCO_3$)	1.97
Gaylussite ($Na_2CO_3 \cdot CaCO_3 \cdot 5\ H_2O$)	0.22
Gypsum ($CaSO_4 \cdot 2\ H_2O$)	−3.32
Halite ($NaCl$)	0.01
Magnesite $MgCO_3$)	0.59
Mirabilite ($Na_2\ SO_4 \cdot 10\ H_2O$)	−0.54
Nahcolite ($NaHCO_3$)	−0.25
Pirssonite ($Na_2CO_3 \cdot CaCO_3 \cdot 2\ H_2O$)	0.42
Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2\ H_2O$)	−0.55

†SI is the saturation index of minerals

Synthesis

In this study an attempt has been made to assess the importance of various sources of salt to the present-day Sambhar lake and also model the evolution of the lake brine based on the evaporation of inflow river and groundwaters. Analysis of rainwater from the region shows that the atmospheric precipitation is only a minor contributor of salt to the lake basin, it only accounts for $\sim$ 3% of the current industrial salt production and less than 1% of the standing crop in the lake following recharge. The chemical analysis of river

and groundwaters from the region are quite saline indicating the general preponderance of evaporite minerals like halite in the area. The evolution of the chemical composition of the Sambhar lake brine during annual cycle of wetting and drying was studied by model simulation using the Hardie-Eugster model. Towards this, several initial endmember waters were evaporated based on the model and their chemical composition compared with those measured in the lake during different seasons. The results show that the evaporative enrichment of lake water collected immediately after the monsoon by and large agrees with the observed chemistry through the annual cycle. The evaporative enrichment of the river and groundwaters though yield brines, their chemical composition and ion ratios differ significantly from the measured values. This suggests that evaporation of pure river and groundwater endmembers cannot produce the observed chemistry of the Sambhar lake brines. Mixing of the river and groundwaters with NaCl (a process likely to occur during wetting cycle of the lake in which salt encrustation would dissolve from the lake bed in the recharging water) and evaporating the mixture water, yields brines whose chemical compositions are in better agreement with those measured. During evaporation of the initial endmember of lake waters viz. river and groundwaters showed saturation with calcite and sepiolite minerals. The presence of some of these minerals such as calcite and dolomite have been identified in the lake sediments. This reaffirms the brine alkaline evolutioary path for the Sambhar lake brine evolution which is consistent the model predicted results.

7.3 Uranium isotopes

Isotopes of uranium (^{238}U, ^{238}U) were measured in the various reservoirs of the Sambhar lake region with a view to understand their geochemical behaviour over a wide range of salinities and also to use uranium as a tracer to infer on the source of salt to the lake. It has been well documented that in oxidizing surface and sub-surface waters ^{238}U is a ubiquitous trace constituent, its mobility being governed primarily by its tendency to form soluble complex ions such as $[UO_2(CO_3)_3]^{4-}$ (Osmond and Cowart,1976). Also, during chemical weathering ^{234}U is fractionated from its parent ^{238}U due to α-recoil effects. This is reflected in the $^{234}U/^{238}U$ activity ratio greater than unity in surface and sub-surface

waters.

The Sambhar lake, its adjacent groundwaters and river waters can be characterized based on ^{238}U abundance in much the same way as was done based on the major ion composition. Both ^{238}U content and $^{234}U/^{238}U$ ratio in the river waters (from Mendha and Roopangarh) and groundwaters exhibit a wide range. The concentration of U and the $^{234}U/^{238}U$ activity ratio in groundwaters range from 3.6 to 71.6 ppb and 1.15 to 1.98, respectively (Table 7.6). The uranium concentration in groundwaters is similar to those reported by Baskaran et al (1986) from the same region.

Table 7.6: U, Ra abundances and $^{234}U/^{238}U$, $^{228}Ra/^{226}Ra$ and $^{210}Po/^{210}Pb$ activity ratios

Water Type	^{238}U Range (ppb)	$^{234}U/^{238}U$ AR@	U/TDS $\mu g\ g^{-1}$	^{226}Ra† $dpm.g^{-1}$	$^{228}Ra/^{226}Ra$ AR	$^{210}Po/^{210}Pb$ AR
River water	12–103	(1.33–2.26)	14–69	(0.11–0.54)	(1–6)	–
Groundwater	3–72	(1.15–1.98)	3–11	(0.11–1.8)	(0.6–2.6)	(0.08–0.73)
Lake water	8–1117	1.64*	0.7–4	$(1.8–6.2)\times10^{-3}$	(2–3)	(1.2–3.0)
Pan water	200–1200	1.62*	3–6	$(1.5–6)\times10^{-3}$	(1.6–2)	2
Sub-surface brine	10–600	1.62**	.05–5	$(4–9.5)\times10^{-3}$	(2–3)	(0.50–0.90)

@ AR is the activity ratio
† concentration normalized to TDS
* average over the annual cycle
** average of several brines

The ^{238}U concentration as a function of TDS for the groundwaters sampled during Feb 92 and Oct 93 is plotted in Fig. 7.11a. The results show a linear trend between U abundance and TDS. Such a trend can be interpreted in terms of a two component mixing - one endmember having low U and low salt content and the other having high U concentration and high TDS. This mixing trend is also evident from the plot of reciprocal concentration of U and $^{234}U/^{238}U$ activity ratio (Fig. 7.11b). A similar mixing trend is observed, though not conclusive, based on the $\delta^{18}O$ and salt content of the groundwaters.

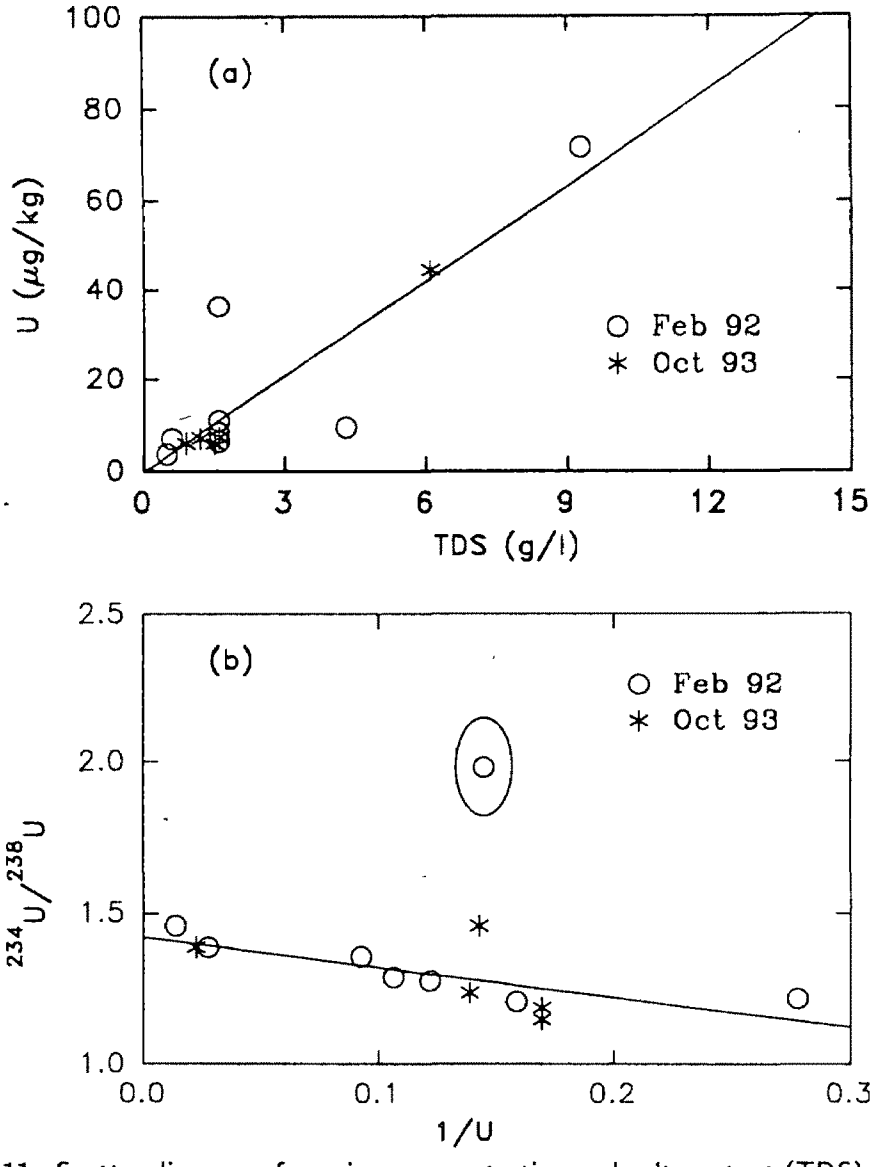
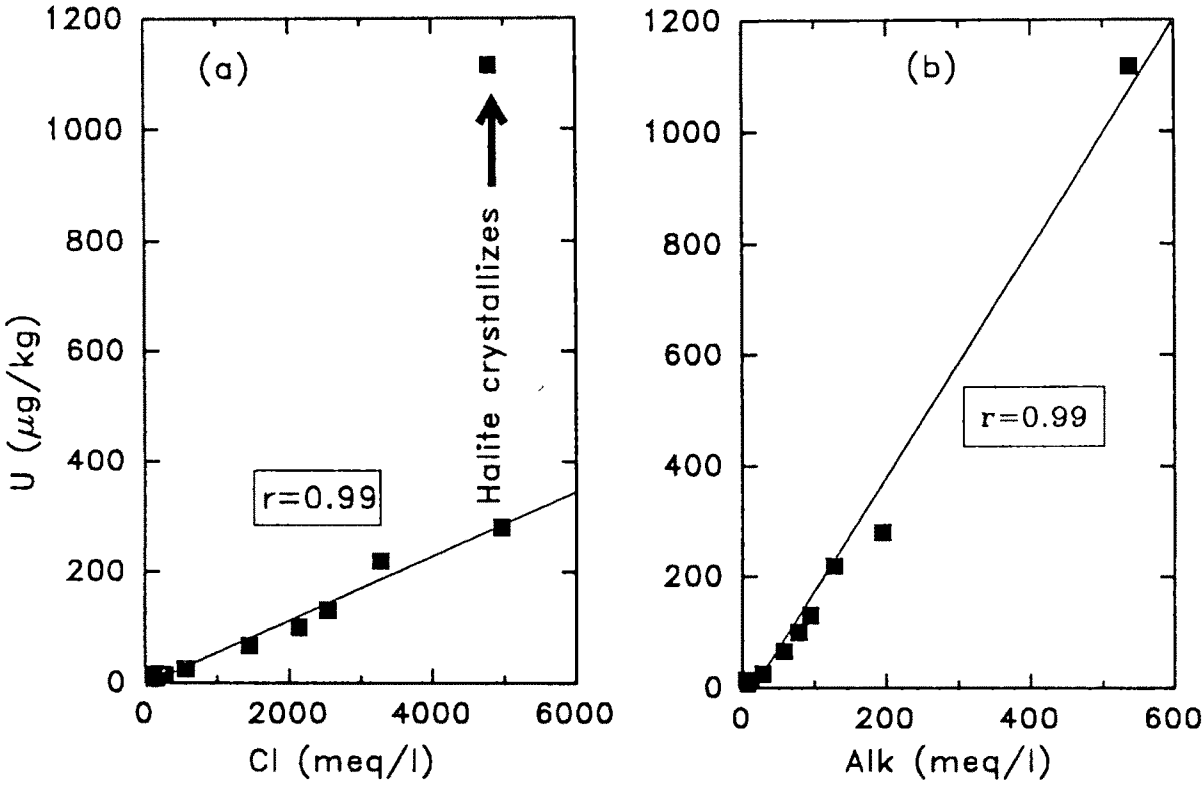


Fig. 7.11a Scatter diagram of uranium concentration and salt content (TDS) in groundwater samples collected during Feb 92 and Oct 93. A linear trend between them is evident. Such relationship can be interpreted in terms of a two component mixing. This inference is also attested by the linear trend between $^{234}U/^{238}U$ and 1/U in Fig. 7.11b. The plot in Fig. 7.11b has been drawn according to Osmond et al,1974, and Osmond and Cowart,1976. The regression line in Fig. 7.11b excludes one encircled data point.



Figures 7.12a and 7.12b: Scatter diagrams of U vs. Cl and U vs. Alk in the Sambhar lake. In Figure 7.12a best fit line has been drawn excluding the data point which corresponds to halite crystallization stage. A strong positive correlation between U and Cl, Alk indicates that U behaves conservative in the lake upto a stage just before the halite crystallization.

In contrast to the groundwaters and river waters, the Sambhar lake waters are characterized by a uniform $^{234}U/^{238}U$ activity ratio, centering around 1.64 (Table 7.6), though the abundance of uranium varies over nearly two orders of magnitude (9–1117 ppb) over the annual cycle. The lowest uranium concentration was measured in samples collected during Oct 92 just after the monsoon season and highest concentration in sample taken during the summer months (May 93). A nearly uniform activity ratio of $^{234}U/^{238}U$ with the large variation in concentration of uranium suggests that behaviour of uranium in lake is influenced by dilution and evaporation processes. This inference is further supported by variation in uranium concentration with Cl and Alk over the annual cycle of evaporation (Fig. 7.12). Both Cl and Alk show a strong positive correlation with the U abundance in the lake basin indicating that their increasing trend is mainly controlled by a common

process of evaporation. In Fig. 7.12a, it is noteworthy that when lake waters reach halite saturation, the U/Cl ratio increases sharply. The information on halite saturation is obtained through the NaCl crystals observed during the brine sampling. The high uranium concentration in residual brine after halite crystallization indicates that U is preferentially retained in the aqueous phase and its concentration rises due to evaporative enrichment.

A unique feature of the Sambhar lake water and sub-surface brine is that both are characterized by the uniform $^{234}U/^{238}U$ activity ratio of 1.62±0.02. This activity ratio is intermediate between the values for the river and groundwater samples (Table 7.6). Such an observation, therefore, suggests that U in the lake basin is derived from the local drainage area and then being recycled within the lake basin. An attempt to derive information on mixing of lake waters with the sub-surface brines using the U isotopes could not be successful because of the constant $^{234}U/^{238}U$ activity ratio (as mentioned above) unlike the inference drawn from the oxygen isotopes.

7.3.1 U–TDS relation: Implication of source of salt to the lake basin

The U concentration in the lake immediately after monsoon is 9 ppb which steadily increases to a value of 1117 ppb during summer. A linear relation exists between U concentration and TDS in the lake (U/TDS ratio ~1.0 μg/g) until the latter reaches a value of 327 g/l after which at TDS of about 360 g/l NaCl begins to precipitate (Fig. 7.13). These results suggest that U concentration and TDS in lake water are intimately coupled and modified only at and beyond halite saturation. It is to be noted that the U/TDS ratio of ~1 μg/g has been observed in lake waters and many sub-surface brine samples which constitute a major source for the current salt production from the lake basin. The U–TDS relation in lake waters has an important bearing on the source of salt to the Sambhar lake. It has been suggested that atmospheric transport and salt deposition from the Rann of Kutch is a source of salt to the lake basin (Holland and Christie, 1909). Results obtained on the U–TDS relation and constancy of the uranium activity ratio during the evaporation cycle suggest that marine aerosols are not an important source of U (and hence salt) to the Sambhar lake.

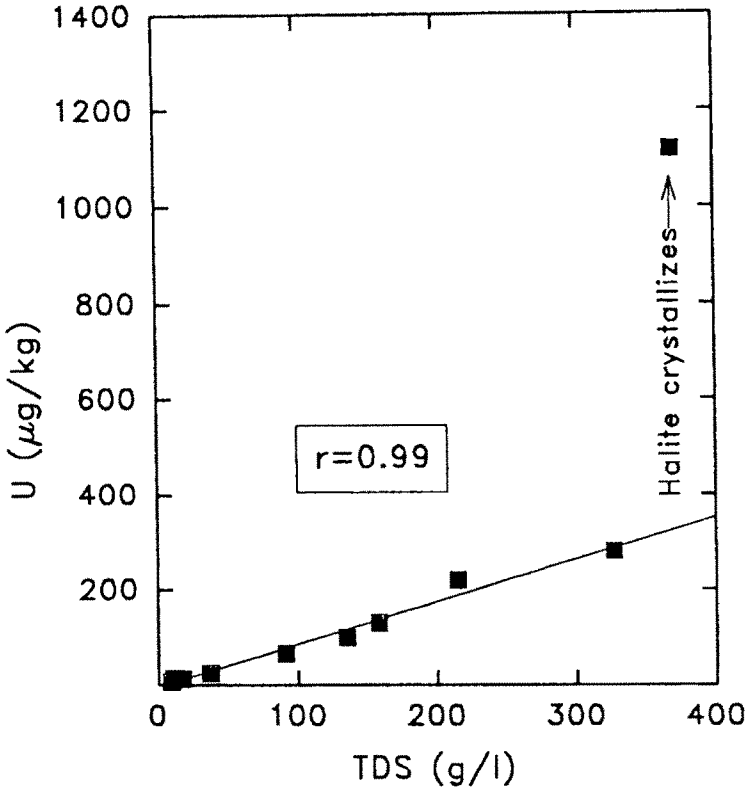


Fig. 7.13 Concentration of uranium in lake waters as a function of salt content (TDS) (i.e. temporal evolution). A strong positive correlation between concentration of uranium and TDS is observed throughout, except during the final stage when halite precipitation occurs. The correlation coefficient (r=0.99) shown is for all the sample points except the one which refers to halite precipitation stage.

If the marine aerosols are not fractionated between uranium and salt, then this result would imply that marine aerosols are not a major source of salt to the Sambhar lake. This is because seawater is characterized by a U/TDS ratio (~0.1 μg/g) and $^{234}U/^{238}U$ activity ratio of 1.14±0.02 (Ku et al,1977; Chen et al,1986), which are distinctly lower than the U/TDS of ~1 and $^{234}U/^{238}U$ of 1.64 in the Sambhar lake. Therefore, if seasalt is a major contributor of U to the lake, it would have reduced U/TDS and $^{234}U/^{238}U$ ratio of the lake water. As this is not observed, it is concluded that the marine aerosols from the Gulf of Kutch are not a major source of U and hence salt to the Sambhar lake. The uranium is probably derived from the weathering of Aravalli granites and schists. The $^{234}U/^{238}U$ activity ratio in Sabarmati river basin which drains through Aravalli is 1.59±0.01 (Borole et al,1979), very similar to that of the Sambhar lake brines.

7.3.2 Fate of uranium in the Sambhar lake

In order to study the fate of uranium in the lake basin, it is essential to know its geochemical behaviour in Sambhar lake waters during evaporation and its association with the end product of the brine i.e. the liquid bittern. It has been discussed above that U in Sambhar lake waters is conservative and its distribution is governed predominantly by dilution/evaporation processes during annual wetting and drying cycle. The high U concentration in lake/pan brines during late stage of evaporation (Figs. 7.12 and 7.13) suggests that U is retained in the aqueous phase. The uranium concentration in bittern (residual brine after halite recovery) is observed to be $\sim$ 3000 μg/l (see Appendix–B, Table 2B) which is about two orders of magnitude higher than the initial lake water value. In an earlier study, Baskaran et al (1986) reported trace concentration of uranium ($\sim$ 0.04 ppb) in the sambhar lake NaCl samples which further supports preferential retention of U in liquid phase of the brine. These results, therefore, indicate that U is not being removed from the lake waters. during the salt production. The concentration of uranium in lake waters was found to be 8.8 μg/l when lake had water depth of 1 meter. Assuming the lake area of about 225 km^2 and 1 m water depth, the amount of uranium recycling in the lake basin is estimated to be 1.98 tons which is consistent with that reported by Baskaran et al (1986).

The present day U/TDS ratio (in μg/g) of lake waters during most of the seasons is $\sim$ 1, which is significantly lower than those measured in the river waters and groundwaters, typically $\sim$ 20 and $\sim$ 5 respectively (Table 7.6). This observation suggests that the U/TDS ratio in the lake is mainly dominated by recycling of the salt from the lake bed during recharge period. Considering the dilution effect on U/TDS ratio due to recycling of the salt, it can be estimated that nearly 95% of the salt is to be added from lake itself in order to bring down the ratio from about 20 (observed in river water) to 1. Such an estimate is consistent with that calculated for the low Na/Cl ratio in lake water compared to the high value in river waters.

7.4 Ra, ^{210}Po and ^{210}Pb nuclides

Studies on the geochemical behaviour of natural radionuclides in sub-surface medium have direct relevance to the management and storage of nuclear wastes. The daughter nuclides of the U-Th series provide useful information of their residence times and retardation characteristics of the aquifer medium. Because of different geochemical properties and varying half lives, the daughter nuclides of the U-Th series serve as in-situ indicators of chemical behaviours for other fission product nuclides injected into the medium. The measurement of Ra, Po and Pb in freshwater and brines from the Sambhar lake region provides opportunity to study their behaviours over wide range of salinities. The concentration of ^{226}Ra in the freshwaters viz. river and groundwaters range between 0.10 to 1.32 dpm/kg which are within the range reported for potable waters from other regions (Hussain,1983). The ^{226}Ra concentration in the pan brines centers around a value of about 0.5 dpm/kg and is nearly independent of salinity in the range $\sim$ 100–400 g/l.

The concentration of ^{226}Ra (normalized to TDS) in groundwaters and river waters ranges from 0.1 to 1.8 dpm/g (Table 7.6), which is about two orders of magnitude higher than that observed in the lake, evaporating pans and sub-surface brines. A possible cause for the low Ra/TDS ratio in the lake and associated brines is that Ra is removed in early stage of brine evolution through co-precipitation with Ca-Mg minerals and during subsequent evaporation (as seen in pan waters) it saturates probably due to equilibration with clay minerals (Fig. 7.14a). The near constancy of Ra concentration over wide range of TDS for the pan waters differ from the trend reported in earlier studies where it showed general increase in concentration with TDS (Kraemer and Reid,1984; Krishnaswami et al,1991). Therefore, in view of the present results, it is suggested that radium may not necessarily show a linear relation with the salt content in chloride brines. The fate of radium in the brine probably depends on the presence of Ca and Mg ions which are controlled by mineral precipitation as discussed in the previous section. The other controlling factor of Ra in solution is the ion-exchange process between the dissolved ions and the clay minerals (Kraemer and Reid,1984). Since all waters in and around the Sambhar lake are saturated with respect to calcite and dolomite minerals, it could be possible that Ra nuclides got removed in the early stage of brine evolution along with the Ca-Mg minerals.

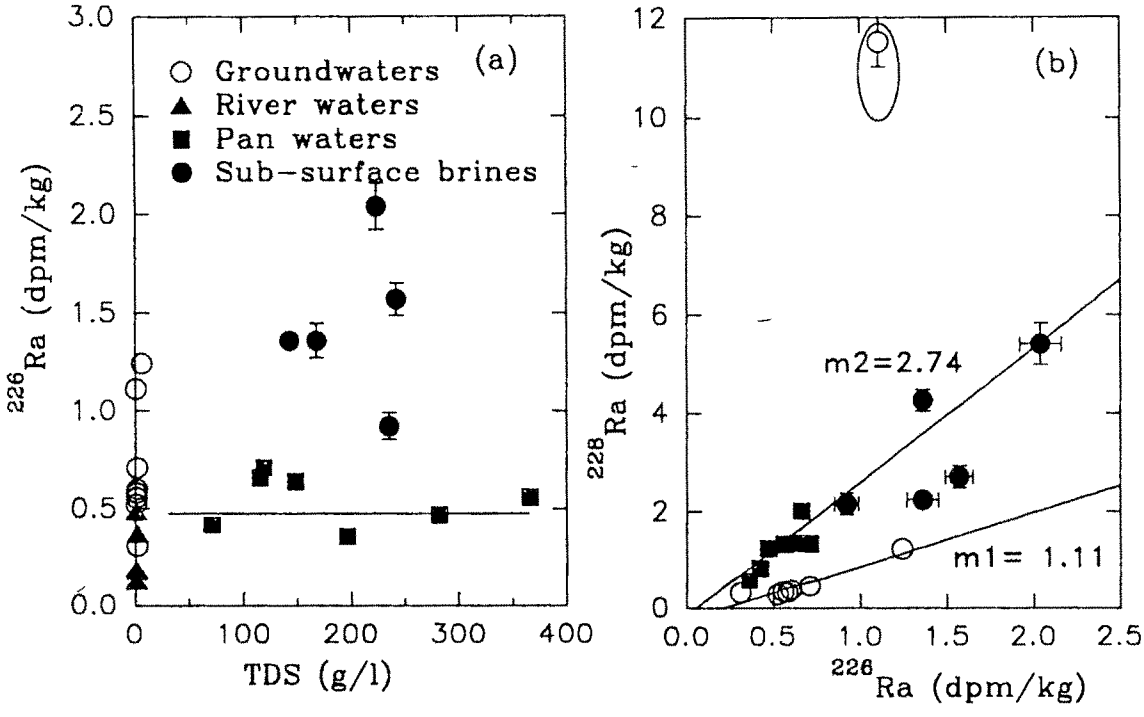


Fig. 7.14a shows relation between radium isotope and the salt content. Despite increase in salt content the radium concentration saturates as shown by an 'eye fit' line implying that the latter possibly equilibrates with the clay minerals. Fig.7.14b indicates a significant positive relation between two radium isotopes although they are supported by different parent nuclides. The slope of the best fit lines through groundwaters (m1) and brines (m2) provides the $^{228}Ra/^{226}Ra$ activity ratio 1.11 and 2.74 respectively.

Since Ra (^{226,228}Ra) is brought into solution by chemical weathering of rocks and α-recoil effects during radioactive decay of their respective parents. A good correlation ($r\sim 0.9$) between ^{226}Ra and ^{228}Ra isotopes has been found (although they are radiogenically supported by different parent nuclides) in both brines and groundwater samples (Fig. 7.14b). The slope of the best fit line for the brine is 2.74 whereas for the groundwaters the slope is 1.11. This indicates that the $^{228}Ra/^{226}Ra$ ratio in these two systems are controlled by different mechanisms. The $^{228}Ra/^{226}Ra$ based on the Th/U weight ratio in soil cores from the region centers around 1.5 (Baskaran et al,1986). Comparing this ratio with that obtained for the brines and groundwaters, it is evident that the Ra isotopes in groundwa-

ters are simply controlled by leaching of the aquifer grains whereas in brines abundance of ^{228}Ra is more than the expected value which could be due to its preferential leaching in high alkaline condition or due to increased α recoil effects. Further study is required to understand the exact mechanism for the high ^{228}Ra/^{226}Ra ratio in the brine. As ^{224}Ra is not measured in various waters, it is difficult to determine the adsorption-desorption characteristics of the nuclides in the aquifer medium (Krishnaswami et al,1982,1991). It is interesting to note that in the Sambhar lake brines, ^{226}Ra abundance is very low which is attributed to removal through mineral precipitation in early stage of brine evolution. If these minerals be identified and separated out from the sediments, then it may be possible to use ^{226}Ra as a chronometer tracer.

The ^{210}Po/^{210}Pb activity ratio in groundwaters from open wells is far less than 1 (observed range is: 0.08−0.73, Table 7.6) indicating preferential removal of ^{210}Po on to particulates. Such an observation is typical of the ^{210}Po and ^{210}Pb systematics in groundwater regimes (Krishnaswami et al,1982; Simpson et al,1982; Dickson and Herczeg,1992). However, in the lake and evaporating pan waters, the ^{210}Po/^{210}Pb ratio is greater than 1 (ranges from 1.2 to 3.0, Table 7.6) which is unlike of the most of the natural waters. This can result from preferential complexation and retention of ^{210}Po in lake/pan waters by algae, being abundant in these waters. In order to understand the role played by algae in complexing ^{210}Po and ^{210}Pb nuclides in these waters, their temporal variations in concentrations of particulate and dissolved phases are required to be known. The sub-surface brines have ^{210}Po/^{210}Pb activity ratio close to equilibrium value which suggest that the reactivity of both the nuclides are similar in this environment.

Synthesis

Studies on U(^{238,234}U), Ra (^{226,228}Ra), ^{210}Po and ^{210}Pb show that U is generally conservative in lake waters over the annual cycle of evaporation; low concentration of Ra/TDS (by about two orders of magnitude) in brines compared to the groundwaters and river waters suggests that Ra isotopes are being removed along with the Ca-Mg minerals in early stage of evaporation and in later stage they saturate probably due to exchange with the clay minerals. The U/TDS ratio in lake waters ($\sim$ 1 μg/g) remains almost constant during the annual cycle of evaporation. Such an observation suggests that U and salt

in the lake are are intimately coupled. It has an important implication to the source of salt in the lake basin. The hypothesis that source of salt to the lake by aeolian transport of marine aerosol particles from the Gulf of Kutch can be ruled out since seawater is characterized by U/TDS ratio $\sim$ 0.1. This is further substantiated if $^{234}U/^{238}U$ activity ratio in lake waters (1.64) is compared with the seawater (1.14$\pm$0.02). The source of salt to the lake by aeolian transport of marine aerosol particles requires that the U/TDS and $^{234}U/^{238}U$ activity ratio in lake waters should reduce to lower side over the annual evaporation period. Furthermore, both these ratios indicate that U and salt in lake basin is continentally derived. When comparison is made for U/TDS ratio (μg/g) among lake waters, adjacent groundwaters (range: 3 to 11) and inflow river waters (range: 14 to 69) it is clear that neither salt nor U is added significantly to the lake either from surface run-off or from the groundwater discharge. This demonstrates that U and salt in the lake basin are self-sustained in the present-day hydrologic set-up.

The distribution of ^{210}Po and ^{210}Pb in various water reservoirs of the lake area indicates their differential behaviours in terms of the particle reactivity. In groundwaters, the $^{210}Po/^{210}Pb$ activity ratio is far less than one which is typical of the groundwater regimes. This indicates that ^{210}Po is removed preferentially onto particulates or on the aquifer grains. However, in sub-surface brines their particle reactivity seems to be equal as they are characterized by $^{210}Po/^{210}$ activity ratio nearly one. However, in lake and evaporating pans the ^{210}Po is retained preferentially over the ^{210}Pb by algae showing $^{210}Po/^{210}Pb$ activity ratio > 1.

Chapter 8

Summary and Conclusions

Summary

This study evaluates relationship among various water reservoirs of the Sambhar lake in terms of their chemical and isotopic composition. In addition, the evolution of brine from evaporation of various initial endmembers of the lake has been studied following the concept of Hardie-Eugster model. The results on $\delta^{18}O$, major ions and radionuclides in lake, atmospheric precipitation, river waters, groundwaters and sub-surface brines are summarized below:

(i) The $\delta^{18}O$ content of the lake and groundwaters sampled during the recharge period overlaps with that of local precipitation (-6.4 to -3.2 $^{o}/_{oo}$) suggesting that oxygen isotopic composition of these reservoirs is dominated by atmospheric precipitation. The annual oxygen isotopic evolution in lake waters is of Rayleigh type and model calculations suggest that isotopically light atmospheric water vapour with $\delta^{18}O$ of about -20 $^{o}/_{oo}$ controls the evolution trend through back condensation during pre and post monsoon months. The $\delta^{18}O$ in sub-surface brines shows a linear increasing trend with TDS which is interpreted in terms of a two component mixing.

(ii) The chemical composition of the Sambhar lake brines and adjacent groundwaters is of Na–Cl type as they constitute more than 70% of the TDS (total dissolved solids). The general dominance of NaCl in the various water reservoirs of the region points to the presence of halite minerals in the drainage basin. Based on NaCl concentration in local rain water, an estimate of the upper limit of salt depositing over whole of the catchment area (~5600 km^2) of the lake through atmospheric precipitation, is ~5000

tons. This estimated amount of salt is less than 1% of the salt inventory present the lake ($\sim 10^6$ tons). Furthermore, study of uranium isotopes in the lake at different stages of annual evaporation suggests that U/TDS (1 μg/g) and $^{234}U/^{238}U$ (1.65±0.03) ratios remain almost constant indicating that neither U nor salt is added significantly to the system by atmospheric transport of salt-laden marine aerosols. (Otherwise, U/TDS and $^{234}U/^{238}U$ ratios would have been reduced since seawater is characterized by U/TDS and $^{234}U/^{238}U$ ratios of 0.1 μg/g and 1.15±0.02 respectively). These results, therefore, discard the hypothesis for the source of salt to the lake through atmospheric transport by the marine aerosols from the Gulf of Kutch.

(iii) Studies on the evolution of the chemical composition of the Sambhar lake brine based on the Hardie-Eugster model and using dilute lake water as the initial endmember, yields brines with composition similar to that measured in the lake in terms of its alkalinity and major ions. The evaporation of pure river water endmember does not produce brine similar to that of the lake brine. The difference lies with the Na/Cl, Na/Alk and Cl/SO_4 ratios. However, one common observation is that the use of dilute lake water and river waters as initial endmembers produce brines which follow an alkaline path (pH increases increases from 8 to about 10). The difference in ion ratios observed in the lake brine and in the calculated brine from the river water evaporation is attributed to recycling of salt from the lake basin during recharge period. The chemical composition of most of the groundwaters in terms of their concentrations for Ca, Mg and alkalinity favours the neutral path of brine evolution following the Hardie-Eugster model. Such brines are neutral contrary to that of the major pool of alkaline brine found in the Sambhar lake. Thus, groundwaters alone cannot account for the chemistry of brines observed in the lake.

(iv) All Sambhar lake water systems viz. river waters, groundwaters, lake waters and sub-surface brines are supersaturated with respect to calcite and dolomite minerals. XRD results showed the presence of calcite and dolomite minerals in the lake sediments which is consistent with the calculated saturation index for these minerals.

(v) The Na/Cl and U/TDS ratios of the river waters differ from those of lake waters. Both these ratios are higher in the river waters compared to the lake. The river waters show an average value of Na/Cl ratio $\sim$ 2.7 and typical U/TDS ratio of $\sim$ 20 μg/g compared to the values of 1.08 and $\sim$1μg/g respectively in the lake. Low Na/Cl and low

U/TDS ratios in the lake compared to the river waters are interpreted in terms of the dilution effect by salt present in the lake basin. An estimate of about 95% of the salt is required to be added from recycling of the salt in the lake basin which can account for the reduction in both Na/Cl and U/TDS ratios of the river waters in the lake. Such an estimate on recycling of the salt is also consistent with that based on the salt input through surface run-off and the total salt inventory of the lake.

(vi) Studies on uranium, radium isotopes, ^{210}Po and ^{210}Pb show that U behaves generally conservative in the lake over the annual cycle of evaporation. Major increase in U/TDS ratio occurs during the late stage of the brine evolution after the halite saturation is reached in the month of May, the peak summer season. Increase in U/TDS ratio beyond halite saturation indicates preferential retention of U in aqueous phase. This aqueous phase gets completely dried up during the summer leaving uranium on the lake bed as a part of salt encrustation. The salt and the uranium becomes available for redissolution during the subsequent wetting period, the monsoon season. Low Ra/TDS ratio (lower by two to three orders of magnitude) in the Sambhar lake brines compared to the groundwaters and river waters suggests that Ra isotopes have been removed since the early stage of brine evolution. Low concentration of Ra is consistent with the low concentrations of Ca and Mg ions in the brine. This indicates removal of radium isotopes probably along with the Ca-Mg minerals. The concentration of ^{226}Ra shows saturation in pan waters in the salinity range of 100 to 370 g/l which is interpreted in terms of equilibration with the clay minerals. Results on ^{210}Po and ^{210}Pb have shown that the former is more efficiently scavenged (onto particulate or aquifer grains) than the latter in groundwaters leading to ^{210}Po/^{210}Pb activity ratio far less than 1. In case of sub-surface brines, these two radionuclides are more or less present in equal activity levels indicating that their reactivities are similar. On the contrary, lake and evaporating pans exhibit ^{210}Po/^{210}Pb activity ratio greater than 1 unlike of many natural waters which has happened due to preferential complexation and retention of ^{210}Po in lake/pan waters by algae.

Conclusions

In the present day hydrologic set-up of the Sambhar lake, the source of water is atmospheric and surface run-off via two major rivers namely Roopangarh and Mendha. The δ^{18}O content of the lake waters during monsoon period (month of July) resembles

very closely to that of the local atmospheric precipitation and groundwaters. Assuming an average depth of 1 m for the lake and average rainfall of 50 cm falling on the lake, the water budget of the lake suggests that one-half of the total lake volume ($\sim 225\times10^9$ ℓ) is contributed by direct precipitation and remaining half by the surface run-off. Based on the NaCl concentration (equivalent of 142 meq/l Cl), the total amount of salt in the lake during Oct 92 is estimated to be $\sim 18.5\times10^5$ tons. Of this, nearly 6% of the salt is transported via river and groundwater sources (based on the geometric mean of Cl concentration 15.8 meq/l for 18 samples). The amount of salt transported through atmospheric precipitation is also relatively insignificant compared to the standing crop of the lake. This illustrates the importance of recycling of salt taking place in the lake basin during recharge period which amounts to nearly 95% of the total salt in the lake. Similar conclusion is also borne out from the low U/TDS ratio measured in the lake water compared to that observed in the river and groundwaters. It is noteworthy that the brine evolution from evaporation of river and groundwater endmembers cannot account for the observed chemical composition of the brine in the lake. Assuming no fractionation between seasalt and uranium, the observed U/TDS and $^{234}U/^{238}U$ activity ratios in the lake brine are significantly different from the seawater values, and hence uranium and salt in the lake basin cannot be coupled to the marine aerosol particles. Thus, the source of salt in the lake via atmospheric transport is limited. Based on these considerations it can, therefore, be concluded that the lake in present day condition is self-sustained and is not influenced significantly by input of salt via atmospheric sources and surface run-off. However, it is quite possible that salt in the lake basin would have formed due to evaporation of a multiple component of source waters viz. river waters, groundwaters and atmospheric precipititaion in the geological past which may explain the resources of salt present in the lake.

Scope of future work

In the present study, water samples from the lake and sub-surface brines were chemically analyzed to arrive at conclusion on their inter-relationships (an indirect method). However, concentration gradients of major ion constituents and isotopic signature of oxygen in interstitial waters of sediment core from the lake during monsoon season may

provide better information of the solute transport and/or water recharge to sub-surface brines. Some of the indirect conclusions e.g. marine vs. nonmarine origin of salt made in the present study can also be verified by the measurement of element B and $\delta^{11}B$ in the lake sediments, lake waters and sub-surface brines (Venghosh et al,1991 and 1992). The distinction between marine and non-marine evaporite deposits in terms of $\delta^{11}B$ lies with its enrichment in marine sediments and seawater relative to the continental crust (boron concentrates in seawater/marine sediments due to isotopic fractionation during its adsorption onto clays). It has been reported that marine evaporite borates are enriched with ^{11}B ($\delta^{11}B$=18 to 31 $^{o}/_{oo}$) relative to non-marine evaporite borates ($\delta^{11}B$=$-$22 to 0 $^{o}/_{oo}$) (Swihart et al,1986). Thus, the issue of marine and non-marine origin of salt in the lake basin can be resolved through the boron isotope measurements.

References

Aggarwal S C (1951) The Sambhar lake salt source, Govt. of India Press, Delhi, pp 365.

Allchin B, Goudie A and Hegde K T M (1978) *The prehistory and paleogeography of the Great Indian desert*, Academic Press, London, pp 370.

Anderson R F, Bacon M P and Brewer P G (1982) Elevated concentrations of actinides in Mono Lake, *Science*, **216**, 514–516.

Baskaran M, Krishnaswami S and Bhandari N (1986) The geochemistry of uranium and thorium isotopes in the salt lakes and adjacent groundwaters of Rajasthan, *J. Geol. Soc. India*, **27**, 90–101.

Bhattacharya B N, Gupta S K, Rishi B P, Mitra A K, and Kashyap V K (1982) Seasonal variation in the composition of Sambhar lake brine and possible origin of its salinity on the salinity problems of the inland lakes of Rajasthan, *Proc. of the workshop on the problems of the deserts in India*, Geol. Surv. of India, Misc. Pub. No. **49**, 80–91.

Biswas R K, Chattopadhyay G S and Sinha Subrata (1982) Some observations on the salinity problems of the inland lakes of Rajasthan, *Proc. of the workshop on the problems of the deserts in India*, Geol. Surv. of India, Misc. Pub. No. **49**, 68–79.

Borole D V, Gupta S K and Krishnaswami S (1979) Uranium isotopic investigations and radiocarbon measurements of river-groundwater systems, Sabarmati basin, Gujarat, India. In: *Isotope Hydrology*, **1**, IAEA.

Bryson R A and Swain A M (1981) Holocene variations of monsoon rainfall in Rajasthan, *Quat. Res.*, **16**, 135–145.

Chen J H, Edward R L and Wasserburg G J (1986) ^{238}U, ^{234}U and ^{232}Th in seawater, *Earth Planet. Sci. Lett.*, **80**, 241–251.

Craig H (1961) Isotopic variations in meteoric waters, *Science*, **133**, 1702.

Craig H and Gordon L I (1965) Deuterium and oxygen-18 variations in the ocean and the marine atmosphere, pp 9–130. In: *Stable isotopes in oceanographic studies and paleotemperatures*, Tongiorgi E (ed.), Consiglio di Geologia Nucleare, Pisa.

Dansgaard W (1964) Stable isotopes in precipitation, *Tellus*, **16**, 436.

Deshmukh G P and Rai V (1991) Some observations on the origin of saline lakes/ranns of Rajasthan, India, *Proc. Quat. landscape of Indian sub-continent*, M S U Baroda (Geology Dept.), 41–47.

Dickson B L and Herczeg A L (1992) Naturally-occurring radionuclides in acid-saline groundwaters around lake Tyrrell, Victoria, *Chem. Geol.*, **96**, 95–114.

Drever J I (1988) Evaporation and Saline waters, pp 232–260. In: *The geochemistry of natural waters*, Printice Hall, Inc., Englewood Cliffs, New Jeresy.

Drever J I and Smith C L (1978) Cyclic wetting and drying of the soil zone as an influence on the chemistry of Groundwater in arid terrains, *Am. J. Sci.*, **278**, 1448–1454.

Epstein S and Mayeda T (1953) Variation of O^{18} content of waters from natural sources, *Geochim. Cosmochim. Acta*, **4**, 213.

Eugster H P (1980) Geochemistry of evaporitic lacustrine deposits, *Ann. Rev. Earth Planet. Sci.*, **8**, 35–63.

Eugster H P and Hardie L A (1978) Saline lakes, pp 237–293. In: *Lakes: Chemistry, Geology, Physics*, A. Lerman(ed.), Springer-Verlag, New York.

Eugster H P and Jones B F (1979) Behaviour of major solutes during closed-basin brine evolution, *Am. J. Sci.*, **279**, 609–631.

Feth J H, Roberon C E, Polzer W L (1964) U S Geological Survey Water Supply Papers, No. 1535I, Washington D C.

Fontes J Ch (1981) Paleowaters. In:*Stable Isotope Hydrology, Deuterium and oxygen-18 in the water cycle*, Gat J R and Gonfiantini R (eds.) IAEA Tech. Rep. Ser. No.**210**, Vienna, pp 273–298.

Garrels R M and Christ C L (1965) *Solutions, Minerals and Equilibria*, Harper and Row, New York, p 450.

Garrels R M and Mackenzie F T (1967) Origin of the chemical composition of some springs and lakes. In: *Equilibrium Concepts in Natural Water Systems, Am. Chem. Soc. Adv. Chem.*, **67**, 222–242.

Gat J R (1981a) Lakes, pp 203–219. In:*Stable Isotope Hydrology, Deuterium and oxygen-18 in the water cycle*, Gat J R and Gonfiantini R (eds.), IAEA Tech. Rep. Ser. No.**210**, Vienna.

Gat J R (1981b) Groundwater, pp 223–238. In:*Stable Isotope Hydrology, Deuterium and oxygen-18 in the water cycle*, Gat J R and Gonfiantini R (eds.), IAEA Tech. Rep. Ser. No.**210**, Vienna.

Gat J R (1981c) Properties of the isotopic species of water: the "isotope effect", pp 7–19. In:*Stable Isotope Hydrology, Deuterium and oxygen-18 in the water cycle*, Gat J R and Gonfiantini R (eds.), IAEA Tech. Rep. Ser. No.**210**, Vienna.

Ghose B (1964) Geomorphological aspects of the formation of salt basins in western Rajasthan, *Proc. UNESCO Symp. on problems of Indian arid zone, Jodhpur*, 79–83.

Godbole N N (1952) The salinity of Sambhar lake, *Proc. Symp. Rajputana Desert, Bull. Nat. Inst. Sci. India*, **1** 89–93.

Gonfiantini R (1981) The δ-notation and the mass-spectrometric measurement techniques, pp 35–84. In: *Stable Isotope Hydrology, Deuterium and oxygen-18 in the water cycle*, Gat J R and Gonfiantini R (eds.), IAEA Tech. Rep. Ser. No. **210**, Vienna.

Gonfiantini R (1986) Environmental isotopes in lake studies, pp 113–163. In: *Handbook of Environmental Isotope geochemistry*, Fritz P and Fontes J Ch (eds.), **2**, the terrestrial envronment, B, Elsevier, New York, NY.

Hardie L A and Eugster H P (1970) The evolution of closed-basin brines, *Mineral. Soc. Amer. Spec. Pap.*, **3**, 273–290.

Harvie C E and Weare J H (1980) The prediction of mineral solubilities in natural waters: The Na–K–Mg–Ca–Cl–SO_4–H_2O systems from zero to high concentration at 25°C, *Geochim. Cosmochim. Acta*, **44**, 981–997.

Harvie C E, Moller Nancy and Weare J H (1984) The prediction of mineral solubilities in natural waters: The Na–K–Mg–Ca–H–Cl–SO_4–OH– HCO_3–CO_3–CO_2–H_2O system to high ionic strengths at 25°C, *Geochim. Cosmochim. Acta*, **48**, 723–751.

Herczeg A L, Simpson H J, Anderson R F, Trier R M, Mathieu G G and Deck B L (1988) Uranium and radium mobility in groundwaters and brines within the Delaware basin, Southeastern New Mexico, U S A, *Chem. Geol. (Isot. Geosci.)*, **72**, 181–196.

Holland T H and Christie W A K (1909) The origin of the salt deposits of Rajputana, *Rec. Geol. Surv. India*, **38(2)**, 154–186.

Hussain N (1983) Behaviour of uranium-thorium series radionuclides in groundwaters : application to study aqifer processes, *PhD thesis*, Guj. Univ., India, pp. 207.

Kraemer T F and Ried D F (1984) The occurrence and behavior of radium in saline formation water of the U. S. Gulf coast region, *Isotope Geoscience*, **2**, 153–174.

Krishnamurthy R V (1984) Stable isotope studies on sedimentary deposits and groundwaters and their climatic implications, *PhD thesis*, pp 127.

Krishnaswami S, Graustein W C, Turekian K K and Dowd J F (1982) Radium, Thorium and Radioactive Lead Isotopes in Groundwaters: Application to the in situ determination of Adsorption–Desorption Rate Constants and retardation factors, *Water Resour. Res.*, **18**(6), 1633–1675.

Krishnaswami S, Bhushan R and Baskaran M (1991) Radium isotopes and ^{222}Rn in shallow brines, Kharaghoda (India), Chemical Geology (Isot. Geosci.), **87**, 125–136.

Ku T L, Knauss K G and Mathieu G G (1977) Uranium in open ocean : Concentration and isotopic composition, *Deep-Sea Res.*, **24**, 1005–1017.

Langmuir D and Riese A C (1985) The thermodynamic properties of radium, *Geochim. Cosmochim. Acta*, **49**, 1593–1601.

Majoube M (1971) Fractionnement en oxygen-18 et en deuterium entre l'eau et sa vapour, *J. Chem. Phys.*, **197**, 1423–1436.

Mathieu G G (1988) Systems for measurement of ^{222}Rn at low levels in natural waters. Health Phys., **55**, 989–992.

Mishra S P (1982) Geochemical evolution of Sambhar salt lake, Jaipur and Nagaur districts, Rajasthan, *Proc. of the workshop on the problems of the deserts in India*, Geol. Surv. of India, Misc. Pub. No. **49**, 92–98.

Moore W S (1976) Sampling Ra-228 in the deep ocean, Deep-Sea Res., **23**, 647–651.

Osmond J K, Kaufman M I and Cowart J B (1974) Mixing volume calculations, sources and aging trends of Floridan aquifer water by uranium isotopic methods, *Geochim. Cosmochim. Acta*, **38**, 1083–1100.

Osmond J K and Cowart J B (1976) The theory and uses of natural uranium isotopic variations in hydrology, Atomic energy review, **144**, 621–679.

Payne B R (1981) Practical applications of stable isotopes to hydrological problems, pp 303–332. In:*Stable Isotope Hydrology, Deuterium and oxygen-18 in the water cycle*, Gat J R and Gonfiantini R (eds.), IAEA Tech. Rep. Ser. No.**210**, Vienna.

Phillips F M, Person M A, and Muller A B (1986) A numerical lumped-parameter model for simulating the isotopic evolution of closed basin lakes, *J. Hydrology*, **85**, 73–86.

Plummer N L, Parkhurst D L, Fleming G W, and Dunkle S A (1988) A computer program incorporating Pitzer's equations for calculation of geochemical reaction in brines, *U. S. Geol. Surv. Water Res. Invest. Rep.* 88–4153.

Ramesh R, Jani R A Bhushan R (1993) Stable isotopic evidence for the origin of salt lakes in the Thar desert, J. Arid Environ, **25**, 117–123.

Sareen J L (1952) Stratigraphic and radiocarbon evidence for the age and development of three salt-lake deposits in Rajasthan, India, *Quat. Res.*, **2(4)**, 496–505.

Sarin M M, Bhushan R, Rengarajan R and Yadav D N (1992) Simultaneous determination of ^{238}U series nuclides in waters of Arabian sea and Bay of Bengal, Indian J. Mar. Sci., **21**, 121–127.

Saxena R K (1987) Oxygen-18 fractionation in nature and estimation of groundwater recharge,*PhD thesis*, Uppsala Univ, pp 152.

Simpson H J, Trier R M, Toggweiler J R, Mathieu G, Deck B L, Olsen C R, Hammond D E, Fuller C and Ku T L (1982) Radionuclides in Mono lake, California, *Science*, **216**, 512– 514.

Singh G, Joshi R D and Singh A B (1972) Stratigraphic and radiocarbon evidence for the age and development of three salt lake deposits in Rajasthan, India, *Quat. Res.*, **2**, 496–505.

Stumm W and Morgan J J (1981) Aquatic Chemistry : An introduction emphasizing chemical equilibria in natural waters, John Wiley and Sons, New York, pp. 780.

Swain A M, Kutzbach J E and Hastenrath S (1983) Estimates of holocene precipitaion for Rajasthan, India, based on pollen and lake-level data, *Quat. Res.*, **19** , 1–17.

Swihart G H, Moore P B and Callis E L (1986) Boron isotopic composition of marine and non-marine evaporite borates, *Geochim. Cosmochim. Acta*, **50**, 1297–1301.

Vengosh A, Chivas A R, McCulloch M T, Starinsky A and Kolodny Y (1991) Boron isotope geochemistry of Australian salt lakes, *Geochim. Cosmochim. Acta*, **55**, 2591–2606.

Vengosh A, Starinsky A, Kolodny Y, Chivas A R, Raab M (1992) Boron isotope variations during fractional evaporation of seawater: New constraints on the marine vs. nonmarine debate, *Geology*, **20**, 799–802.

Yurtsever Y and Gat J R (1981) Atmospheric waters, pp 103–139. In:*Stable Isotope Hydrology, Deuterium and oxygen-18 in the water cycle*, Gat J R and Gonfiantini R (eds.), IAEA Tech. Rep. Ser. No.**210**, Vienna.

Wasson R J, Smith G I and Agrawal D P (1984) Late quaternary sediments, minerals and inferred geochemical history of Didwana lake, Thar desert, India, *Paleogeog., Paleocli., Paleoeco*, **46**, 345–372.

White D E, Hem J D and Waring G A (1963) Chapter F. Chemical Composition of Subsurface waters. In: *Data of Geochemistry*, U S G S Prof. Pap. 440–F, Washington D C.