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Geo-chemical Behavior of Uranium in the Sambhar Salt Lake, Rajasthan (India): Implications to "Source" of Salt and Uranium "Sink"

D. N. Yadav · M. M. Sarin

Abstract   Among several salt lakes in the Thar Desert of western India, the Sambhar is the largest lake producing about 2×10^5 tons of salt (NaCl) annually. The "lake system" (lake waters, inflowing river waters, and sub-surface brines) provides a unique setting to study the geo-chemical behavior of uranium isotopes (^{238}U, ^{234}U) in conjunction with the evolution of brines over the annual wetting and evaporation cycles. The concentration of ^{238}U and the total dissolved solids (TDS) in lake water increase from ~ 8 μg L^{-1} and ~ 8 g L^{-1} in monsoon to $\sim 1,400$ μg L^{-1} and 370 g L^{-1}, respectively, during summer time. The U/TDS ratio (~ 1 μg g^{-1} salt) and the ^{234}U/^{238}U activity ratio (1.65 ± 0.05), however, remain almost unchanged throughout the year, except when U/TDS ratio approaches to 3.8 at/or beyond halite crystallization. These observations suggest that uranium behaves conservatively in the lake waters during the annual cycle of evaporation. Also, uranium and salt content (TDS) are intimately coupled, which has been used to infer the origin and source of salt in the lake basin. Furthermore, near uniform ratios in evaporating lake waters, when compared to the ratio in seawater (~ 0.1 μg g^{-1} salt and 1.14 ± 0.02, respectively), imply that aeolian transport of marine salts is unlikely to be significant source of salt to the lake in the present-day hydrologic conditions. This inference is further consistent with the chemical composition of wet-precipitation occurring in and around the Sambhar lake. The seasonal streams feeding the lake and groundwaters (within the lake's periphery) have distinctly different ratios of U/TDS (2–69 μg g^{-1} salt) and ^{234}U/^{238}U (1.15–2.26) compared to those in the lake. The average U/TDS ratio of ~ 1 μg g^{-1} salt in lake waters and ~ 19 μg g^{-1} salt in river waters suggest dilution of the uranium content by the recycled salt and/or removal processes presently operating in the lake during the extraction of salt for commercial use. Based on mass-balance calculations, a conservative estimate of "uranium sink" (in the form of bittern crust) accounts for

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~ 5 tons year^{-1} from the lake basin, an estimate similar to its input flux from rivers, i.e., 4.4 tons year^{-1}.

1 Introduction

Among several salt lakes in the Thar Desert of western India, the Sambhar is the largest lake producing about 2×10^5 tons of salt (NaCl) annually. The "lake system" (lake waters, inflowing river waters and sub-surface brines) provides a unique setting to study the geo-chemical behavior of uranium isotopes (^{238}U, ^{234}U) in conjunction with the evolution of brines over the annual wetting and drying cycles. As a part of our geo-chemical study of the Sambhar Salt Lake, we have attempted to model the chemical and U-isotope evolution of lake brines that constrains the source of salt and uranium in the lake basin in present-day hydrologic set-up. Earlier study with the application of U–Th series radionuclides, was carried out for the three saline lakes of Rajasthan, viz., Sambhar, Didwana, and Kuchaman including the adjacent groundwaters (Baskaran et al. 1986). Their data and results were lacking in terms of seasonal samplings over the annual cycle of evaporation. With the improvement in our sampling strategy, it was possible to identify qualitatively the Sambhar lake brine evolutionary path from the freshwater end-members (Yadav et al. 2007). Major ion data resulted in the estimation of inventory of salt (NaCl), $\sim 10^6$ tons, along with the riverine and aeolian inputs of flux 6×10^4 and 5×10^4 tons year^{-1}, respectively. The results indicated that the majority of salt is derived from the recycling and re-solution of salt encrustation from the lake bed during recharge period (Yadav et al. 2007). In addition, the results of particle reactive nuclides (^{226,228}Ra, ^{210}Po and ^{210}Pb) were interestingly distinct to define the saline lake water systems (evaporating lake/pan brines and sub-surface brines) geo-chemically and isotopically different from the adjacent groundwaters of the lake (Yadav and Sarin 2009).

This article presents comprehensive data on uranium isotopes (^{238}U, ^{234}U) in conjunction with the TDS (total dissolved solids) in the Sambhar lake over its annual wetting and drying cycles (1992–1993). The adjacent groundwaters and shallow sub-surface brines were also investigated in different seasons to study their seasonal variability and to establish any possible geo-chemical relation with the evaporating lake waters. River water samples were analyzed for evaluating the mobility and fate of uranium isotopes in the lake basin. These data provide useful information to place constraints on the origin and source of salt to the lake basin, hitherto lacking in the literature.

2 Hydrogeology and Climate of Study Area

The Sambhar Salt Lake is a shallow centripetal lake situated at 26°52′–27°2′ N, 74°53′–75°13′ E (Fig. 1). It is located at an elevation of 360 m above the mean sea level, having an area of ~ 225 km^2 and an average depth of ~ 1 m. It is a closed sedimentary basin receiving an average annual rainfall of 50 cm (Swain et al. 1983; Yadav 1995, 1997) over its catchment area of $\sim 5,600$ km^2 (Biswas et al. 1982). The lake is fed by a number of seasonal streams, the Roopangarh, Mendha, Kharain, and Khandel, constituting centripetal drainage system of ephemeral type (Aggarwal 1951; Biswas et al. 1982; Roy 1999). The
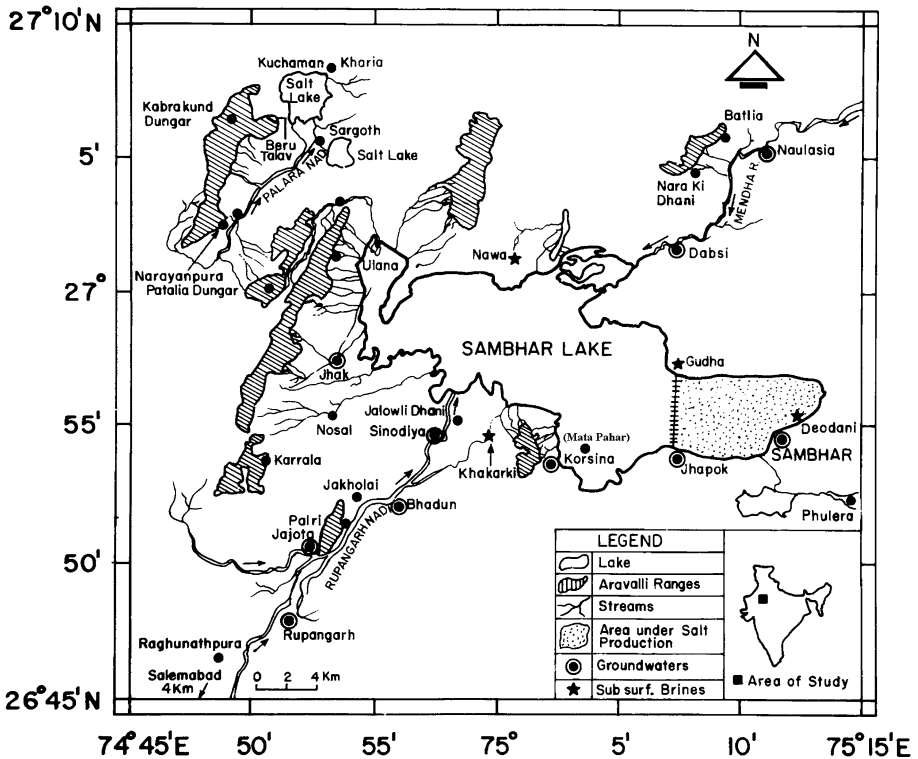
Fig. 1 Map showing the sample locations in the Sambhar lake. The groundwater wells are indicated by *encircled point* and sub-surface brine wells are shown by *asterisk* symbol. Additional sub-surface brine samples are also collected at a distance of 50–100 m from those marked locations. Shallow groundwater samples (1–2 m deep) from the river bed are taken to be representative of river waters

water-balance study in the lake using oxygen isotopes suggests it to be a "terminal lake" in which inflow during the SW monsoon (July–Sept.) balances the evaporation during October–June, leaving almost negligible residual water in the peak summer (Ramesh et al. 1993; Yadav 1997).

The lake basin, bounded by the wind-blown sand dunes, is formed by the neo-tectonism (Sinha-Roy 1986; Deshmukh and Rai 1991; Roy 1999). The major lineament controlling the neo-tectonic activity is along the NE–SW direction. About 2×10^5 tons of NaCl is manufactured annually both from the Sambhar lake and sub-surface brines occurring at shallow depths (~ 3–4 m below the lake bed). The origin of salt in the lake basin has been a subject of scientific interest since the last century. The various hypotheses proposed include: (1) dissolution of salt from halite beds (relict of Tethys sea) within the basin (Godbole 1952), (2) weathering of country rocks followed by evaporation (Aggarwal 1951), and (3) aeolian transport of salt-laden aerosol particles from the Gulf of Kutch by SW monsoon winds (Holland and Christie 1909). Among these, the first hypothesis characterizes the "internal" source while the others two are "external" sources of salt to the lake basin. Roy 1999 had proposed concept of stream trapping in the geological past and existence of paleo-river channels as one of the possible causes of present-day salinity in the lake.

The principal source of water to the lake basin is atmospheric precipitation followed by surface run-off through seasonal streams during the SW monsoon (Yadav 1997). It is

estimated from the annual average atmospheric precipitation (~ 50 cm) and average water depth of Sambhar lake (~ 1 m) that half of the lake water is from atmospheric precipitation and remaining half is from the surface run-off. The inflow of water from streams occurs only for a few days during the SW monsoon. These streams drain through Pre-Cambrian schists, phyllites, and slates. Groundwater tables adjacent to the lake show a significant hydraulic gradient toward the lake (Karanth 1964); however, recent studies indicated them to be isolated water bodies (Yadav 1997; Yadav et al. 2007). The observed chemical and isotopic composition of lake brine, based on dissolved major ions and oxygen isotopes data, preclude groundwaters to be major source of water to the lake in present-day hydrologic set up. The predicted brine evolution from most of the groundwaters is neutral Na–Cl type in contrast to the observed highly alkaline (pH > 9.5) Na–Cl type of brine in the lake. Within the close vicinity of lake, these groundwaters show considerable variation in the salinity indicating their recharge from different sources with variation in salt dissolution during their passage through aquifer medium (Karanth 1964; Yadav 1995).

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°C and May is the hottest month with maximum temperature range of 39–41°C. The maximum average relative humidity during the monsoon season is about 76% 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). Thus, it is evident that the lake waters undergo maximum evaporation during the period Mar–May over the annual cycle.

3 Lake Deposits and Sedimentary Environments

The Sambhar lake depression consists mainly of sedimentary deposits in the form of horizontally bedded silt (Aggarwal 1951). Such silt deposition varies in thickness over the lake bed ranging from 22 m deep in the center (near Mata Pahar hill, Fig. 1) to 3–5 m at the shores. Mostly the silt formation is argillaceous with considerable amount of mica; however, at some places hard and calcareous material is also reported. Salt resources of the lake are the impregnated brines in this silt formation. Recent sediment core study from the Sambhar lake by Sinha and Raymahashay 2004 revealed clastic and non-clastic evaporite minerals representing fluctuation in paleoenvironmental conditions during its Quaternary evolutionary history. The clastic fraction of lake sediment contained quartz, alkali feldspar, mica, chlorite, amphibole, and weathering products such as kaolinite and goethite. The non-clastic evaporite fraction was dominated by calcite and halite. At deeper depths of sediment profile, thin layer of gypsum was found whereas shallower depth represented an assemblage of thenardite, kisserite, and polyhalite. Such an observation was interpreted with varying geo-chemical conditions that favored a change in brine evolutionary path during its evolutionary history. Their studies have indicated that the geo-chemical evolution of Sambhar lake has spanned for a period more than 30 ka.

In the present-day hydrologic set-up of the lake, its eastern side (Fig. 1) is isolated and being extensively utilized for salt production by pumping of both lake water and shallow sub-surface brine and subjecting to solar evaporation. On the lake bed, 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. In the process of salt production, significant amount of residual salt in the form of bittern liquid, and crust consisting of

mainly NaCl, Na_2CO_3, and Na_2SO_4 is disposed off on the lake bed. It is very likely that such salt-deposited material undergoes re-cycling and re-solution during the recharge period of the lake, i.e., during the SW monsoon. The main lake reservoir qualifies to be oxidizing environment as there was no observation of pungent or foul smell (emission of methane or H_2S) from the lake basin. In contrast, evaporating pans having bittern liquid and bittern crust evidenced such smell indicating qualitatively to be reducing environments. Such environmental conditions are critical in regulating the geo-chemical behavior of uranium isotopes and other redox sensitive elements in the lake basin.

4 Sampling and Experimental Techniques

Several sampling trips were undertaken to collect river waters, groundwaters, as well as lake waters and samples of sub-surface brines. Sampling locations are shown in Fig. 1, and sample details were published elsewhere (Yadav et al. 2007). Major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations were measured by the flame AAS, alkalinity (hereafter abbreviated as Alk) and Cl^- by titrimetery, and SO_4^{2-} by gravimetry in brine samples. In rain and groundwater samples, ion chromatographic technique was used for Cl^- and SO_4^{2-} ions. The individual ion concentrations were summed up to get the TDS content in the samples (Yadav 1995; Yadav et al. 2007). For uranium measurement, large volume water samples (10–20 l) were collected from river and groundwaters, whereas 25–250 ml of sample was adequate in case of saline lake waters and brines. The river and groundwater samples were filtered through 0.45-μm Gelman cartridge filters, acidified in the field with HNO_3 to pH ∼ 2 followed by addition of Fe-carrier and ^{232}U yield tracer. After 6–8 h of equilibration, uranium isotopes were co-precipitated along with $Fe(OH)_3$ (Sarin et al. 1992). In the laboratory, uranium was separated on an ion-exchange column (AG-1X8, 100–200 mesh) in 9 M HCl and then purified on a similar column in 7 M HNO_3. The purified fraction containing uranium isotopes was electroplated on Pt discs, and their activities were assayed on silicon-surface barrier detectors coupled to a pulse height analyzer (Sarin et al. 1992). In lake waters and brines, U was determined directly on samples (filtered through Whatman 54 filter papers) by evaporating and digesting with HNO_3 in presence of ^{232}U yield tracer. The chemical yield for uranium in groundwater samples centered around 75% whereas that in the brines, it ranged between 30 and 80%.

5 Results and Discussion

The TDS, pH, Alk, U concentration, U/TDS ratio, and $^{234}U/^{238}U$ activity ratio for various water samples collected from the lake and adjacent water bodies, and their locations with sampling periods are given in Table 1. Synthesis of data in the form of range and their mean values are presented in Table 2. The errors given for uranium concentration and $^{234}U/^{238}U$ activity ratio in Tables 1 and 2 correspond to $\pm 1\sigma$, calculated from counting statistics and uncertainty of tracers/spikes calibrations and blank corrections. The results for major ion composition (pH, cations, and anions) have been published and reported elsewhere (Yadav et al. 2007). The major findings of hydrogeochemical study have revealed an inter-relation between lake water and sub-surface brines. The sub-surface brines, which form the major source for the current salt production, owe their origin to the evaporating lake waters (Yadav et al. 2007). In addition, characteristically, among the various water samples, river waters generally had lower TDS, (range 0.5–2.0 g L^{-1});

Table 1 Isotopic composition of Uranium, salt contents, and alkalinity of Sambhar Lake waters

Sample code/ sampling season	Location	TDS (g L^{-1})	pH	Alk (meq L^{-1})	U (µg L^{-1})	U/TDS (µg g^{-1} salt)	^{234}U/^{238}U (Activity ratio)
River waters							
SL #82 (Oct. 93)	Sinodiya	1.2	8.1	9.2	25.6 ± 1.3	21.33	1.99 ± 0.04
SL #83 (Oct. 93)	Bhadun	0.9	8.0	12.4	13.0 ± 0.5	14.44	2.26 ± 0.05
SL #84 (Oct. 93)	Rupangarh	0.6	8.0	8.1	11.9 ± 0.4	19.83	1.88 ± 0.04
SL #85 (Oct. 93)	Dabsi	1.9	7.8	10.3	40.8 ± 1.5	21.47	1.39 ± 0.02
SL #86 (Oct. 93)	Naulasia	1.5	8.6	12.4	103.8 ± 4.4	69.20	1.33 ± 0.02
Groundwaters							
SL #10 (Feb. 92)	Gudha	1.6	7.9	4.4	8.2 ± 0.2	5.12	1.28 ± 0.02
SL #90 (Oct. 93)		1.2	8.0	5.4	7.0 ± 0.2	5.83	1.26 ± 0.03
SL #17 (Mar. 92)	Sambhar Town	9.3	7.5	7.6	71.6 ± 2.4	7.69	1.46 ± 0.04
SL #88 (Oct. 93)		6.1	7.8	6.5	44.4 ± 1.2	7.27	1.39 ± 0.02
SL #18 (Mar. 92)	Jhapok	1.6	7.9	6.8	36.2 ± 1.5	22.62	1.39 ± 0.02
SL #20 (Mar. 92)	Korshina	0.6	7.8	7.5	6.9 ± 0.2	11.5	1.98 ± 0.03
SL #21 (Mar. 92)	Sambhar Town	1.6	7.3	5.8	6.3 ± 0.2	3.94	1.21 ± 0.02
SL #91 (Oct. 93)		1.5	7.5	5.9	5.9 ± 0.2	3.93	1.19 ± 0.04
SL #24 (Mar. 92)	Sambhar Town	4.3	7.2	6.1	9.4 ± 0.1	2.19	1.29 ± 0.02
SL #22 (Mar. 92)	Sambhar Town	1.6	7.2	3.9	10.8 ± 0.3	6.75	1.36 ± 0.01
SL #92 (Oct. 93)		1.6	7.4	4.9	7.2 ± 0.2	4.5	1.24 ± 0.03
SL #23 (Mar. 92)	Sambhar Town	0.5	7.2	4.2	3.6 ± 0.1	7.2	1.22 ± 0.02
SL #87 (Oct. 93)		0.9	8.4	4.9	5.9 ± 0.2	6.55	1.15 ± 0.03
SL #65 (Feb. 93)	Jhak	12.3	–	11.3	57.2 ± 1.7	4.65	1.78 ± 0.03
SL #66 (Feb. 93)	Jajota	3.2	–	10.3	21.3 ± 0.6	6.65	1.67 ± 0.03
Lake water							
SL #46 (Oct. 92)	Jhapok	8.6	8.5	7	9.1 ± 0.4	1.06	1.66 ± 0.07
SL #47 (Oct. 92)	Gudha	8.8	8.5	7	8.2 ± 0.3	0.93	1.67 ± 0.06
SL #52 (Oct. 92)	Mata Pahar	9.3	8.2	7	9.3 ± 0.3	1.0	1.71 ± 0.06
SL #55 (Feb. 93)	Jhapok	17.5	–	12	14.8 ± 0.5	0.85	1.63 ± 0.06
SL #69 (Apr. 93)		36.7	–	28	26.9 ± 0.8	0.73	1.61 ± 0.03
SL #72 (Apr. 93)		37.7	-	28	26.9 ± 0.8	0.71	1.63 ± 0.04
SL #73 (Apr. 93)		91.3	–	58	70.8 ± 2.3	0.77	1.68 ± 0.03
SL #74 (May 93)		135	–	78	109.3 ± 3.1	0.81	1.62 ± 0.03
SL #75 (May 93)		158	–	94	143.7 ± 4.6	0.91	1.66 ± 0.03
SL #76 (May 93)		215	–	127	250.5 ± 7.4	1.16	1.65 ± 0.03
SL #78 (May 93)		327	–	194	342 ± 12	1.05	1.65 ± 0.03
SL #79 (May 93)		370	–	537	1397 ± 41	3.78	1.66 ± 0.02
Sub-surface brine							
SL #9 (Feb. 92)	Gudha	143	8.8	100	433 ± 13	3.03	1.53 ± 0.03
SL #11 (Feb. 92)	Gudha	223	9.1	250	737 ± 22	3.29	1.59 ± 0.03
SL #12 (Feb. 92)	Gudha	109	8.8	85	548 ± 17	5.03	1.64 ± 0.03
SL #13 (Feb. 92)	Gudha	235	9.1	272	391 ± 10	1.66	1.60 ± 0.02
SL #14 (Feb. 92)	Deodani	168	9.4	184	219 ± 7	1.3	1.61 ± 0.04

Table 1 continued

Sample code/ sampling season	Location	TDS (g L^{-1})	pH	Alk (meq L^{-1})	U (µg L^{-1})	U/TDS (µg g^{-1} salt)	^{234}U/^{238}U (Activity ratio)
SL #15 (Feb. 92)	Deodani	242	9.1	261	287 ± 8	1.19	1.62 ± 0.03
SL #42 (Oct. 92)		195	9.5	179	196 ± 6	1.0	1.66 ± 0.04
SL #58 (Feb. 93)		196	–	211	285 ± 10	1.45	1.61 ± 0.03
SL #16 (Feb. 92)	Deodani	235	9.1	244	225 ± 6	0.96	1.60 ± 0.03
SL #43 (Oct. 92)		147	9.7	101	107 ± 3	0.73	1.65 ± 0.04
SL #59 (Feb. 93)		205	–	172	176 ± 5	0.86	1.57 ± 0.03
SL #45 (Oct. 92)	Deodani	165	9.5	152	126 ± 5	0.76	1.67 ± 0.06
SL #60 (Feb. 93)		179	–	160	237 ± 7	1.32	1.62 ± 0.02
SL #49 (Oct. 92)	Main Line	240	8.3	82	25 ± 1	0.1	1.63 ± 0.07
SL #57 (Feb. 93)		265	–	78	12 ± 0.5	0.04	1.66 ± 0.07
SL #56 (Feb. 93)	Main Line	258	–	255	122 ± 3	0.47	1.50 ± 0.03
SL #70 (Apr. 93)		264	–	260	138 ± 6	0.52	1.61 ± 0.06
SL #63 (Feb. 93)	Khakarki	77	–	10	200 ± 8	2.59	1.65 ± 0.04
SL #71 (Apr. 93)	Nawa	221	–	305	500 ± 14	2.26	1.77 ± 0.03

– not available

the groundwaters around the lake show a wide variation in TDS, ranging from 0.5 to 12 g L^{-1}. The salinity of lake water including concentration of uranium varies by orders of magnitude over the annual evaporation cycle. Residual lake water (as a function of lake level) has been estimated over the annual evaporation cycle (1992–1993) based on TDS measurements, shows an inverse relation with the exponential rise in uranium concentration (Fig. 2). The change in lake level, as mentioned in Sect. 3, is partly due to extensive evaporation and partly due to pumping of lake water in evaporating pans/kyars being used for salt production. In conjunction with salinity data, results on abundance of uranium and ^{234}U/^{238}U activity ratio in various water bodies have been discussed and presented below in terms of the source of "salt" and "sink" for uranium in the present-day hydrologic set-up.

5.1 Uranium Isotopes

The Sambhar Salt lake, adjacent groundwaters, and river waters can be characterized based on their U abundance and ^{234}U/^{238}U activity ratios. Both the ^{238}U content and ^{234}U/^{238}U activity ratio in 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 4 to 72 µg L^{-1} and 1.15 to 1.98, respectively (Table 2), similar to those reported by Baskaran et al. 1986 from the same region. In river waters, uranium concentration and its activity ratio varies from 12 to 104 µg L^{-1} and 1.33 to 2.26, respectively (Table 2). The U/TDS ratio in river waters ranged from 14 to 69 µg g^{-1} salt (average ∼19 µg g^{-1} salt, excluding one data point with a ratio of 69) and that in groundwater ranges from 2 to 23 µg g^{-1} salt (average ∼6 µg g^{-1} salt, excluding the two high values of 11.5 and 22.6, Tables 1 and 2). The data for groundwaters show a linear trend between U abundance and TDS and between 1/^{238}U and ^{234}U/^{238}U activity ratios (Fig. 3a, b). Such a trend can be interpreted in terms of a two-component mixing from within groundwater system—one end-member having low U and low salt content and the other having high U concentration

Table 2 Synthesis of data for salt content (TDS), ^{238}U, and $^{234}U/^{238}U$ activity ratio in Sambhar lake water samples

Sample	TDS (g L^{-1}) Range	^{238}U (μg L^{-1}) Range	$^{234}U/^{238}U$ (AR)			U/TDS (μg g^{-1} salt)		
			Range	Mean	Standard deviation	Range	Mean	Standard deviation
River waters	0.5–2.0	12–104	(1.33 ± 0.02)–(2.26 ± 0.05)	1.88[a], $n = 4$	0.36	14–69	19.3	2.9
Groundwaters	0.4–12	4–72	(1.15 ± 0.03)–(1.98 ± 0.03)	1.35, $n = 13$	0.18	2–23	5.6	1.6
Lake waters	9–376	8–1,400	(1.61 ± 0.03)–(1.71 ± 0.06)	1.65[b], $n = 11$	0.03	0.7–4	0.9[d]	0.1
Sub-surface brine	39–270	10–600	(1.50 ± 0.02)–(1.77 ± 0.06)	1.62[c], $n = 19$	0.06	0.04–5	1.5	1.2

AR activity ratio

[a] Average of four samples excluding the one, SL#86

[b] Average over the annual cycle for 11 samples (range: 1.61–1.71)

[c] Average of 19 sub-surface brine samples (range: 1.50–1.67)

[d] Excludes data points at/beyond halite precipitation
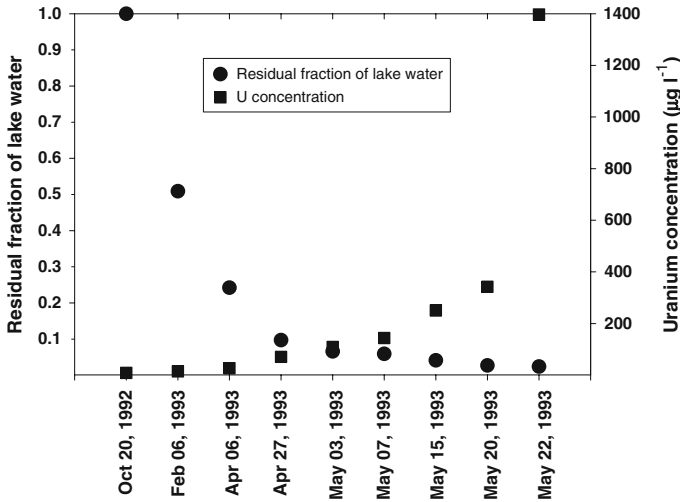
Fig. 2 Scatter plot showing relation between lake level (residual fraction of lake water) and uranium concentration during annual wetting and drying cycles (1992–1993)

Fig. 3 a, **b** Scatter diagram for U versus TDS and $^{234}U/^{238}U$ versus 1/U salt content (TDS) in groundwater samples collected during Feb–Mar. 92 and Oct. 93 showing both temporal and spatial variations. A linear trend in Fig. 2b is interpreted in terms of a two-component mixing (Osmond et al. 1974 and Osmond and Cowart 1976). The *regression line* in Fig. 3b excludes one encircled data point for better presentation of data
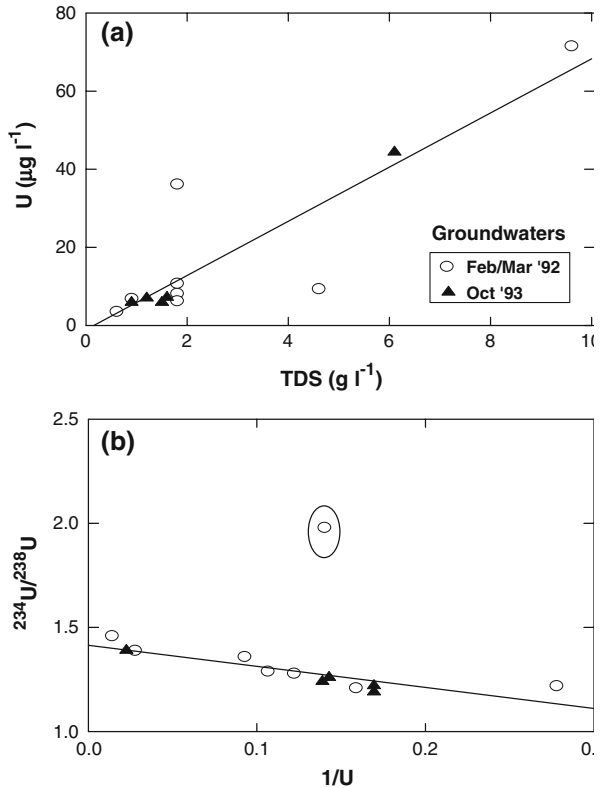
and high TDS. This is further attested by the linear trend between ^{234}U/^{238}U isotope ratio and reciprocal of uranium content in groundwaters (Fig. 3a, b) following the concept of Osmond et al. 1974 and Osmond and Cowart 1976. The two end-member mixing trend, as stated above, "within groundwater" system has also been inferred based on the δ^{18}O and salt content of groundwaters (Yadav 1995, 1997).

In contrast, the Sambhar lake waters are characterized by a uniform ^{234}U/^{238}U activity ratio throughout the year, centering around 1.65 ± 0.05 (weighted mean, Table 2), although the abundance of uranium varies over nearly two orders of magnitudes (8–1,400 μg L^{-1}) over the annual cycle of evaporation. The lowest uranium concentration was measured in samples collected after the monsoon (during October) and the highest in samples collected during the summer months (May). Furthermore, the uranium concentration shows linear increase with alkalinity and chloride over the annual cycle of evaporation (Fig. 4b). It is, however, noteworthy (Fig. 4a) that when lake waters exceed halite saturation, the U/Cl ratio increases sharply. Similarly, the uranium concentration rises linearly with the salt content (TDS) over the annual evaporation cycle until halite mineral crystallizes, beyond which the uranium concentration rises exponentially (Fig. 4c). All these observations suggest that behavior of uranium in the Sambhar lake is conservative all through the season from recharge period (July–Sep) to extreme evaporation (month of May). These data also show that uranium remains in brine even after halite precipitation. In fact, presence of halite crystals was observed in the brine sample (SL #79, Table 2) during sampling. A positive saturation index (SI), 0.11, calculated for halite for this sample further attests to NaCl removal at TDS ~370 g L^{-1} (Yadav et al. 2007). A linear relation between U and Alk even at the late stage of evaporation beyond halite crystallization (Fig. 4b) further substantiates our above inference. Uranium gets removed only in solid bittern crust as has been discussed in the next section.

A unique feature of the Sambhar lake water and sub-surface brines is that both have a uniform and high ^{234}U/^{238}U activity ratio of 1.65 ± 0.05 in all the seasons. Such an observation indicates strong evidence for inter-relation between evaporating lake brines and sub-surface brines. In fact, sub-surface brines get recharged from lake water/meteoric
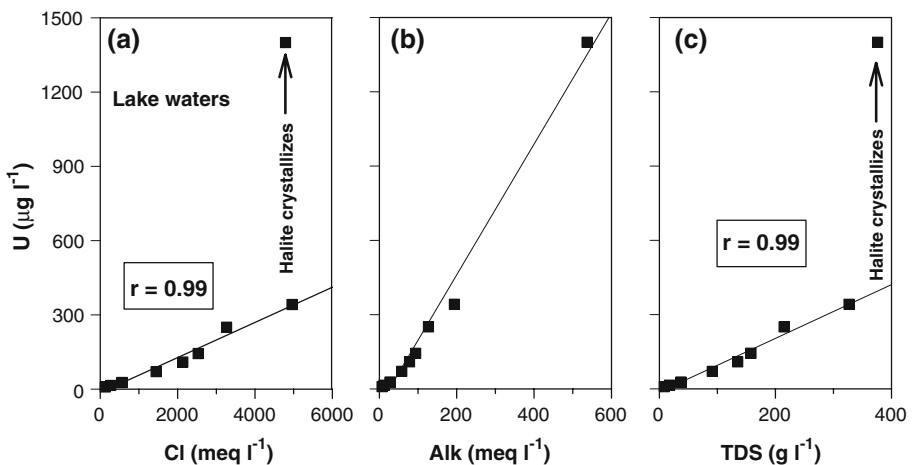

Fig. 4 a–c Scatter diagrams of U versus Cl, U versus Alk, and U versus TDS in the Sambhar lake representing annual evaporation cycle. In Fig. 4a and c the best fit lines are drawn excluding the data point which corresponds to halite crystallization stage. A strong positive correlation between U, Cl, Alk, and TDS indicates that U behaves conservatively in the lake up to a stage just before halite crystallization

precipitation during monsoon season and thereafter by a process aided by pumping activity used for salt production. Such inference was drawn in our earlier study using evolution of conservative tracer (oxygen isotopes) in the evaporating lake waters (Yadav 1997). The activity ratio of uranium, 1.65 ± 0.05, is intermediate between the values for the river and groundwater samples (range: 1.15–2.26, Tables 1 and 2). The high ^{234}U/^{238}U activity ratio in surface and sub-surface waters generally results from weathering of igneous rocks, which preferentially release ^{234}U. The high ^{234}U/^{238}U in waters of the Sambhar lake system most likely results 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. The high concentration of ^{238}U in many of these waters (>10 µg L^{-1}) is difficult to be explained in terms of congruent weathering of the rocks, as it would require solute of several grams of rock per kg of water, which is highly unlikely. The high ^{238}U, therefore, has to result either from (i) its concentration by evaporation over time and the recharge of the aquifers on the lake bed with these brines or (ii) weathering of uranium deposits. The second alternative seems unlikely, as it may be difficult to obtain the ^{234}U/^{238}U activity ratio of ∼1.65. It is, thus, inferred that weathering of Aravalli rocks and onset of aridity in Rajasthan predominantly influence the ^{238}U abundance and ^{234}U/^{238}U activity ratio of Sambhar lake system. Attempt to derive information on mixing of lake waters with the sub-surface brines using U isotopes was not successful as the ^{234}U/^{238}U activity ratio in both reservoirs was nearly the same. This is unlike the methodology and inferences drawn from the oxygen isotope study (Yadav 1995, 1997).

5.2 U–TDS Relation: Implication to Source of Salt in the Lake

The results on uranium isotopes in conjunction with TDS and NaCl content of various water reservoirs of the Sambhar lake have been used to place constraints on the source of salt in the lake basin in the present-day hydrologic set up. The major ion concentrations of various water reservoirs in and around the Sambhar lake suggest a general provenance of halite (NaCl) or dissolution of desiccated salt minerals (Yadav 1995; Yadav et al. 2007). The inventory of salt (NaCl) in the lake water after the freshwater input (during monsoon) is about 10^6 tons based on 1-m average depth, ∼225 km^2 surface area of lake, and ∼9 g L^{-1} as NaCl concentration in lake water (Yadav 1995; Yadav et al. 2007). The atmospheric deposition of NaCl via precipitation over the entire catchment area of the lake is estimated to be about 5,000 tons based on NaCl content (∼2 mg L^{-1}) of rain waters (Yadav 1995). As the samples were collected in close vicinity of the lake, this estimate could be an upper limit arising due to re-suspension of NaCl from the lake bed during dry weather and subsequent wash-out by rain waters. However, the above estimate is ≤3% of the current salt production and <1% of the total salt inventory. The adjacent groundwaters do not seem to influence the lake salinity as mentioned earlier in Sect. 2. Their chemical composition do not favor the type of brine composition observed in the lake (Yadav et al. 2007). This is further supported from the findings that the saline lake system (lake water and sub-surface brines) and groundwaters are two geo-chemically distinct regimes based on Ra–Po–Pb isotope systematics (Yadav and Sarin 2009). On the other hand, riverine input of salt to the lake is estimated to be about 3% of the salt inventory of the lake and 30% of the current salt production (Yadav et al. 2007). Therefore, the estimates of salt from local precipitation and surface run-off suggest that atmospheric deposition is not the major source of salt to the lake. The contribution of salt from the surface run-off could be considered substantial in geologic time scale. Repetitive drying and wetting cycles over long periods of time have resulted in vast reserve of salt in the form of impregnated brine

in shallow aquifers just below the lake bed. We have attempted here to substantiate some of our findings on the origin and source of salt and placed constraints on the issues of marine versus non-marine origins based on U/TDS and $^{234}U/^{238}U$ activity ratios measured in lake waters, as presented below.

Results on U isotopes and TDS in lake waters during annual wetting and drying cycles show a general conservative behavior for U. A linear relation exists ($r = 0.99$) between U concentration and TDS in the lake (U/TDS ratio ~ 1.0 µg g^{-1} salt) until the latter reaches a value of 327 g L^{-1}, beyond which NaCl precipitates at TDS content of about 370 g L^{-1} (Fig. 4c). Following halite precipitation, U/TDS ratio increases to values as high as ~ 4 µg g^{-1} salt (Fig. 4c). These results suggest that U concentration and TDS in lake waters are intimately coupled and modified only at/or beyond halite saturation. It is also noteworthy that many sub-surface brines (Fig. 1; Table 2) exhibit U/TDS ratios (µg g^{-1} salt) in the range of 2–5 similar to the values observed in evaporating lake waters at halite saturation stage. Such an observation suggests that the sub-surface brines, the major source of current salt production from the lake bed, are caused by infiltration and recharge to the underlying strata under extreme aridity condition prevailing over the region.

It has been suggested (Holland and Christie 1909) that atmospheric transport of salt during summer from the Rann of Kutch is a source of salt to the lake basin. Results on the U–TDS relation and $^{234}U/^{238}U$ activity ratio during the annual cycle of evaporation can serve to place constraints on the wind-borne atmospheric deposition of salt to the lake. This is because seawater is characterized by a U/TDS ratio (~ 0.1 µg g^{-1} salt) and $^{234}U/^{238}U$ activity ratio of 1.14 ± 0.02 (Ku et al. 1977; Chen et al. 1986; Sarin et al. 1994). Assuming that marine aerosols are not fractionated with respect to uranium and salt, the results obtained in this study, viz., constancy of U/TDS of ~ 1 µg g^{-1} salt and $^{234}U/^{238}U$ activity ratio of 1.65 over the annual cycle, imply that marine aerosols are not a major source of salt and/or uranium to the Sambhar lake. Nevertheless, a rough estimate on the sea-salt-uranium contribution can be made based on the two end-member mixing calculation (Faure 1986). Here, the one component is lake water during the recharge period (i.e. monsoon season) and the other is sea-salt with their respective U/TDS ratios. It has been conservatively estimated that sea-salt contribution to lake salinity is about 2%. There could be limitation in use of U/TDS ratio in lake water at or beyond halite crystallization, as the ratio increases sharply from about ~ 1 to 4 (µg g^{-1} salt) (Table 1; Fig 4c). However, such situation occurs at final stage of evaporation only when halite crystallizes, otherwise does not. Thus, during the study period on an annual scale, the aeolian sea-salt mixing to the lake could be taken as about 2%, which is very too low to sustain vast reservoir of salt in the lake basin. In the geologic time scale, the aerosol contribution could be significant in controlling the lake salinity. However, the marked difference in the observed $^{234}U/^{238}U$ activity ratio between seawater and Sambhar lake brines precludes the possible marine origin of salt to the lake basin. Thus, based on this analogy, it is difficult to ascertain the source of lake salinity as that due to the marine aerosol transport by SW monsoon wind.

5.3 Fate of Uranium in the Sambhar Salt Lake: Material Balance Study

As discussed above, uranium in the Sambhar lake is conservative and that its distribution is predominantly governed by dilution and evaporation processes during annual wetting and drying cycles. The high U concentration in lake brines during late stage of evaporation (Fig. 4) suggests that U is retained in the aqueous phase. The uranium concentration in bittern (residual brine after halite recovery) is observed to be $\sim 3,000$ µg L^{-1}, about two orders of magnitude higher than the initial lake water value. In an earlier study, Baskaran

Table 3 Uranium contents and isotope ratios in Sambhar Lake evaporite samples

Sample type	TDS (g L^{-1})	Sample size	U content	^{234}U/^{238}U	Reference
Bittern liquid	392	25 ml	2,965 μg L^{-1}	1.63 ± 0.02	This study
Bittern crust	–	2.3 g	2,700 μg kg^{-1}	1.63 ± 0.03	This study
Halite	–	NA[a]	0.04 μg kg^{-1}	NA[a]	Baskaran et al. (1986)

– Not applicable

[a] NA not available

et al. 1986 reported trace concentration of uranium ($\sim$0.04 μg kg^{-1} salt) in the Sambhar lake NaCl samples which further supports preferential retention of U in liquid phase of the brine. The abundance of uranium and isotope activity ratio observed in end products of evaporating lake water, viz., bittern liquid, bittern solid crust, and pure halite are presented in Table 3. These results, therefore, indicate that U is not removed from the lake waters during the brine evolution and salt crystallization stages; however, it gets removed in bittern crust, an evaporative end-product of bittern liquid (Table 3).

A steady-state annual mass-balance equation for uranium inputs to the lake water during its recharge and, subsequently, its discharge to sub-surface brines and removal from the system as "sink" can be represented by

$$V_{RLW} \cdot [U]_{RLW} + V_{AP} \cdot [U]_{AP} + V_{RW} \cdot [U]_{RW} - V_{SSB} \cdot [U]_{SSB} - \text{sink} = 0 \qquad (1)$$

where the terms on the left side of equation represent input fluxes from the residual lake water (the first term), overhead atmospheric precipitation (the second term), output fluxes from discharge to sub-surface brine (the third term), and artificial removal as "sink" (the final term). A simple schematic box-model representing all the input and output fluxes has been shown in Fig. 5. The definitions and values of each term in Eq. 1 are shown in Table 4. With some valid and reasonable assumptions, Eq. (1) can be solved to estimate the annual input and output fluxes of uranium in the Sambhar Salt lake during a complete wetting and drying cycles. Here, an assumption is made based on discussion in Sect. 5.2 that the aeolian contribution of salt or uranium to the lake is insignificant, and thus the second term in Eq. (1) is neglected. Various simplified terms from Table 4 in Eq. (1) are used to get input fluxes of uranium to the Sambhar lake as about 4.4 tons year^{-1} by riverine sources and 7.6 tons year^{-1} by the residual lake water. Similarly, the output flux of uranium recharged to sub-surface brines is estimated to be about 7 tons year^{-1} and artificial removal rate of uranium as "sink" (bittern crust) is about 5 tons year^{-1}. On the one hand, an important information from this calculation is obtained, that is, there is an
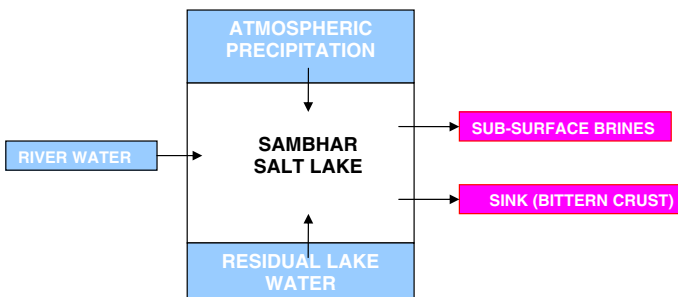

Fig. 5 Schematic box model showing sources and sinks of uranium in Sambhar Salt Lake, Rajasthan, India

Table 4 The definition and values used in mass-balance calculation for uranium in Sambhar Salt Lake, Rajasthan (India)

Terms	Definition	Simplified term	Value	Unit	Reference
V_{RLW}	Volume of residual lake water in extreme evaporation just before monsoon season (derived from ratio of average TDS during recharge, 8.9 to 370 g L^{-1} during extreme evaporation, Table 1)	$0.024*V_{LW}$	5.4×10^9	L	Yadav (1997) and Yadav et al. (2007)
V_{AP}	Volume of atmospheric precipitation over lake area during recharge period	$0.5*V_{LW}$	$\sim 112.5 \times 10^9$	L	Yadav (1995) and Yadav et al. (2007)
V_{RW}	Volume of lake recharged by river waters during monsoon	$0.5*V_{LW}$	$\sim 112.5 \times 10^9$	L	Yadav (1995) and Yadav et al. (2007)
V_{SSB}	Volume of sub-surface brine recharged from the lake during annual cycle	$0.12*V_{LW}$	27×10^9	L	Yadav (1997)
V_{LW}	Volume of lake water during recharge period, i.e., during monsoon	–	225×10^9	L	Yadav (1995) and Yadav et al. (2007)
$[U]_{RLW}$	Uranium concentration in residual lake water, SL #79, Table 1	–	1,400	µg L^{-1}	This study
$[U]_{AP}$	Uranium concentration in atmospheric precipitation derived from sea salt over lake area	–	Negligible	µg L^{-1}	This study
$[U]_{RW}$	Average uranium concentration in river waters	–	39	µg L^{-1}	This study
$[U]_{SSB}$	Average uranium concentration in sub-surface brines	–	261	µg L^{-1}	This study
Sink	Artificial removal rate of uranium from the lake in the form of bittern crust[a]	–	~ 5	Tons year^{-1}[b]	This study

[a] The solid bittern crust is an end-product of evaporating lake brines, which contains essentially halite (NaCl) besides carbonate and sulphate minerals such as trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), thenardite ($Na_2SO_4$) and burkeite ($2\ Na_2SO_4 \cdot Na_2CO_3$) including significant amount of uranium (Yadav 1995)

[b] 1 ton = 10^6 g

equilibrium between the input flux of uranium from the residual lake water (which becomes the source for the following monsoon) and that discharged to sub-surface brines. On the other hand, riverine input flux of uranium is higher by a factor of 2 as compared to its annual inventory of 2 tons (based on average uranium concentration and average depth of lake). This clearly indicates a net loss of U from the lake basin. Such loss of uranium is related to its artificial removal in the form of bittern crust. Owing to extensive salt production activity, the bittern crust is being sold and supplied to Fertilizer Company such as Sarkar Fertiliser Ltd, Ballarpur in large scale by M/s Sambhar Salt Ltd (SSL). The high output flux of uranium as "sink" derived from Eq. 1 is further corroborated by the high uranium content of a bittern crust sample (2,700 µg kg^{-1}, Table 3). Such an observation

has implication in terms of lowering of U/TDS ratio in lake water, $\sim 1\ \mu g\ g^{-1}$ salt, during most of the sampling period except during the peak summer. The observed U/TDS ratio in lake water is very low as compared to the inflowing river waters ($\sim 19\ \mu g\ g^{-1}$ salt). The low value of U/TDS in lake water could be explained partly as due to removal through bittern crust and partly through recycling of encrusted salt from the lake basin during recharge period. An alternate sink of U in lake could be through co-precipitation with calcareous minerals in sediments. In an earlier study, the Th/U weight ratio was determined for soil cores taken from the lake bed, which did not indicate preferential uptake of U in sediments (Baskaran et al. 1986). Thus, the possibility of uranium removal through co-precipitating calcareous minerals in sediments can be taken as minimal.

6 Summary and Conclusions

The study of uranium and isotopic ratio (^{234}U/^{238}U) places some constraint on the origin and source of salt to the lake basin. The U/TDS ratio and two end-member mixing calculations for uranium concentration in sea-salt and that in lake waters during recharge period (monsoon season) are made use of to reveal that marine aerosols are not a major source of salt to the Sambhar lake. A conservative estimate based on this approach accounts for annual 2% of present-day lake salinity by sea-salt/marine aerosols. Likewise, the salt input to the lake basin by atmospheric precipitation and surface/sub-surface run-off is 1–2 orders of magnitudes lower than the total inventory of salt ($\sim 10^6$ tons) in the lake. All these estimates are based on the built-in assumptions and annual supply of uranium and salt to the lake basin in present-day hydrologic set-up. The situation could be different if rates of annual supply of uranium and salt through wind-borne routes be extrapolated to geological time scales; in that case, the accumulated salt could be significant. However, with the observed difference in activity ratio of ^{234}U/^{238}U between sea water (1.14 ± 0.02) and lake waters (surface and sub-surface brines, 1.65 ± 0.05), the hypothesis for the wind-borne and/or marine origin of uranium can be considered unrealistic. Similarly, based on a close relation observed between uranium concentration and salt content (TDS) in evaporating lake waters, the origin of salt from marine source can be considered unrealistic. The relationships studied for U versus TDS and 1/U versus ^{234}U/^{238}U A.R. in the groundwaters (adjacent to the lake) show linear trends suggesting a two-component mixing "within groundwater system". Such an observation is consistent with the earlier findings based on oxygen isotope study (Yadav 1997).

The mass-balance calculation for uranium in Sambhar lake indicates that the riverine input to the lake is higher than the lake inventory by a factor of about 2 reflecting its removal as a "sink". This is further supported by a relatively low U/TDS ratio in lake waters as compared to groundwaters and river waters. Due to enhanced current salt production (2×10^5 tons year^{-1}), there is increased generation of by-product of salt i.e., bittern crust, a material containing sulphate, carbonate, and uranium. The bittern crust has been identified as a potential "sink" for uranium in Sambhar lake. A conservative estimate based on the mass-balance analysis reveals that uranium is being removed at the rate of about 5 tons year^{-1}. This estimated removal flux of uranium is similar to the input flux from riverine source, i.e., 4.4 tons year^{-1}. The estimated discharge flux of uranium in sub-surface brines, 7.5 tons year^{-1}, is in equilibrium with the input flux from the residual lake water. Such an observation may have an important implication to vast reserve for uranium in the Sambhar lake sub-surface brines, which could be used for commercial exploitation.

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