

# **Radium isotopes and Rare Earth Elements in Indian Rivers and the Bay of Bengal**

A THESIS

Submitted for the Award of Ph. D degree of

***Mohan Lal Sukhadia University, Udaipur, India***

In the Faculty of Science

By

**R. Rengarajan**



Under the Supervision of

**Prof. S. Krishnaswami**

Physical Research Laboratory

**Planetary & Geosciences Division**

Physical Research Laboratory, Navrangpura, Ahmedabad, India-380 009.

**Mohan Lal Sukhadia University, Udaipur**

Year of submission: 2004

# Contents

List of tables

List of figures

Acknowledgements

Statement

## Part A. Radium isotopes in the Bay of Bengal and the Arabian Sea

<b>Chapter 1</b>	<b>Introduction</b>	<b>1-4</b>
1.1	Introduction	2
1.2	Ocean circulation	3
1.3	Measurement of Ra isotopes	4
<b>Chapter 2</b>	<b>Methods and approaches</b>	<b>5-23</b>
2.1	Introduction	6
2.2	Oceanographic features of the western Bay of Bengal	6
2.3	Oceanographic features of the Arabian Sea	13
2.4	Sample sites, collection and analytical methods	17
2.4.1	Sampling of Ra isotopes in the Bay of Bengal and the Arabian Sea	17
2.4.2	Onboard measurements	19
2.4.3	Analysis of Ra isotopes	21
<b>Chapter 3</b>	<b>Ra isotopes in seawater</b>	<b>24-63</b>
3.1	Introduction	25
3.2	Marine chemistry of Ra isotopes	25
3.3	Relation of Ra isotopes with salinity	26
3.3.1	Bay of Bengal	26
3.3.2	Arabian Sea	30
3.4	Advection-diffusion modeling of surface Ra isotopes	35
3.4.1	One-dimensional lateral model	35
3.4.2	Two-dimensional lateral model	38
3.4.2.1	2-D diffusion model	39
3.4.2.2	2-D advection model	44
3.4.2.3	Error analysis	45
3.4.2.4	2-D advection-diffusion model	45
3.5	Advection-diffusion modeling of water column $^{228}\text{Ra}$ profiles	48
3.5.1	1-D vertical diffusion model	52
3.6	Conclusions	52

## Part B. Rare Earth Elements and Uranium in the Yamuna and the Chambal rivers

<b>Chapter 4</b>	<b>Introduction</b>	<b>64-72</b>
4.1	Introduction	65
4.2	Geochemistry of uranium	65
4.3	Geochemistry of Rare Earth Elements	67
4.4	Distribution of REE in river water	69
4.5	Distribution of REE in river sediments	69
4.6	Motivation for this study	71

<b>Chapter 5</b>	<b>Methods and approaches</b>	<b>73-110</b>
5.1	Introduction	74
5.2	The Yamuna river catchment	74
5.2.1	Geologic setting of the Yamuna river catchment	74
5.2.2	Major rivers of the Yamuna river catchment	76
5.2.3	Climate of the Yamuna river catchment	78
5.3	The Chambal river catchment	84
5.3.1	Geologic setting of the Chambal river catchment	84
5.3.2	Major rivers of the Chambal river catchment	85
5.3.3	Major river valley projects in the Chambal basin	86
5.3.4	Climate of the Chambal river catchment	90
5.4	Sample sites, collection and analytical methods	91
5.4.1	Sampling of the Chambal and the Yamuna river water and bed sediments	91
5.4.2	Analysis of bed sediments	92
5.4.3	Analysis of river water	101
<b>Chapter 6</b>	<b>REE in the Yamuna and the Chambal rivers</b>	<b>111-185</b>
6.1	Introduction	112
6.2	Major ions and REE in the dissolved phase	113
6.2.1	Major ions in the Chambal river	113
6.2.2	Sources of major ions in the Chambal river	128
6.2.2.1	Silicate weathering	129
6.2.2.2	Carbonate weathering	132
6.2.2.3	Weathering rates and CO <sub>2</sub> consumption rates	133
6.2.3	REE river water chemistry	135
6.2.4	Gadolinium anomalies in river waters	148
6.3	Major element and REE composition of bed sediments	149
6.3.1	Major and trace elements	149
6.3.2	REE transport in stream sediments	156
6.3.3	Enriched fraction of trace and rare earth elements	176
6.4	Conclusions	180
<b>Chapter 7</b>	<b>U isotopes in the Yamuna and the Chambal rivers</b>	<b>186-213</b>
7.1	Introduction	187
7.2	Dissolved uranium in the Chambal and the Yamuna river systems	189
7.3	Sources of uranium to the Yamuna & the Chambal rivers	199
7.4	Variation in uranium isotope ratios	201
7.5	Uranium weathering rates	211
7.5	Anthropogenic input of uranium	211
7.6	Conclusions	212
<b>Chapter 8</b>	<b>Synthesis and scope for future research</b>	<b>214-221</b>
8.1	Important results of this study	215
8.1.1	Ra isotopes in the ocean	215
8.1.2	U and REE in the Yamuna and the Chambal rivers	216
8.2	Scope of future research	219
<b>References</b>		<b>222-241</b>
<b>List of Publications</b>		<b>242</b>

# List of Tables

Table		Page
2.1	Gamma counting efficiencies for the HPGe well detector	22
3.1	Range and mean concentrations of $^{228}\text{Ra}$ and $^{226}\text{Ra}$ and $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio of the surface waters of the Arabian Sea and the Bay of Bengal	32
3.2	Effective eddy diffusivities using lateral transects from the shore of the Bay of Bengal	38
3.3	List of GEOSECS stations reoccupied during FORV Sagar Sampada cruises	48
3.4	Effective vertical eddy diffusivities using depth profiles of $^{228}\text{Ra}$	52
A3.1	Concentration of Ra isotopes, temperature and salinity of the surface waters of the Bay of Bengal	54
A3.2	Concentration of Ra isotopes, temperature and salinity in the water column profiles	57
4.1	Nuclear data for uranium isotopes	66
4.2	Basic REE data	67
5.1	Small streams and tributaries of the Yamuna catchment	81
5.2	ICP-AES specification and operating conditions	97
5.3	Comparison of the reported and measured values of REE in rock standards	97
5.4	Comparison of concentrations of REE in the sediment samples measured by ICPAES and INAA	103
A5.1	Sampling details of the Chambal river catchment	106
A5.2	Bed sediment and dissolved U sampling details of the Yamuna river catchment	107
A5.3	Sampling details of the river water samples for REE	109
6.1	Major ion composition of the headwater streams of the Chambal river	115
6.2	Range and mean concentrations of major ions of the samples of the Chambal river	116
6.3	Average concentration of major ions in rainwater	129
6.4	Moles of ions released into solution per mole of mineral	131
6.5	Comparison of the two methods used in calculating silicate and carbonate contribution of total cations	133
6.6	Fluxes of total dissolved salts and chemical denudation rates	135
6.7	REE concentrations of the Yamuna and Chambal river waters	140
6.8	Dissolved $\Sigma\text{REE}$ , $\Sigma\text{LREE}$ , $\Sigma\text{HREE}$ , $\text{La}_{\text{CN}}/\text{Yb}_{\text{CN}}$ and Ce and Eu anomalies of the Yamuna and Chambal river water samples.	142
6.9	Range and mean concentrations of REE and Eu, Ce and Gd anomalies in the Yamuna and the Chambal river waters	143
6.10	Inter-element correlation matrix for the river water samples from the Yamuna and the Chambal catchment	145
6.11	$\text{CaCO}_3$ , $\text{C}_{\text{Org}}$ , major elements and trace elements in bed sediments from the Chambal watershed and Ganga River	150

6.12	Range and mean concentrations of major and trace elements of the Chambal river sediments	151
6.13	Range and mean concentrations of REE in the Yamuna and the Chambal river bed sediments	160
6.14	Comparison of REE contents in sediments of various rivers	162
6.15	$\Sigma$ REE, $\Sigma$ LREE, $\Sigma$ HREE, $(La/Yb)_{CN}$ and Ce and Eu anomalies of the Yamuna and Chambal river bed sediments	163
6.16	Range and mean concentrations of chondrite normalized ratios and Eu and Ce anomalies of the sediments from the Yamuna and the Chambal river catchments	165
A6.1	Rare Earth Element concentrations data of bed sediments from the Yamuna and Chambal rivers and their tributaries	183
7.1	Concentrations of uranium isotopes and $^{234}U/^{238}U$ activity ratios of the Yamuna River water samples	190
7.2	Range and mean values for dissolved uranium and $^{234}U/^{238}U$ activity ratio in the Yamuna and the Chambal river.	192
7.3	Temporal variation in the Ganga, Yamuna and Chambal uranium chemistry	195
7.4	Dissolved uranium concentrations and uranium weathering rates in the Yamuna and the Chambal rivers compared with the major Indian rivers.	206

## List of figures

Figure		Page
2.1	River water inputs to the Bay of Bengal	8
2.2	A schematic representation of currents during SW and NE monsoons	9
2.3	Map showing bathymetric contours and mean annual surface salinity in the Bay of Bengal	11
2.4	Surface water mass regions of the Indian Ocean based on water type diagrams	13
2.5	Mean annual surface salinity of the Arabian Sea	14
2.6	Sampling of seawater onboard FORV Sagar Sampada	18
2.7	Map showing sample locations for Ra isotopes	20
2.8	Calibration curve for HPGe well detector	22
2.9	Typical gamma spectra of background, sample and U and Th standards	23
3.1	Isotopes of uranium and thorium decay series showing the lineage of Ra isotopes	26
3.2	Frequency plot $^{226}\text{Ra}$ in the surface waters of the Bay of Bengal	27
3.3	$^{228}\text{Ra}$ and $^{226}\text{Ra}$ concentrations in the Bay of Bengal surface waters	28
3.4	Plots of $^{228}\text{Ra}$ , $^{226}\text{Ra}$ and $[228/226]$ as a function of salinity in the surface waters of the western Bay of Bengal	31
3.5	Frequency plot $^{226}\text{Ra}$ in the surface waters of the Arabian Sea	32
3.6	$^{228}\text{Ra}$ and $^{226}\text{Ra}$ concentrations in the Arabian Sea surface waters	33
3.7	Plots of $^{228}\text{Ra}$ , $^{226}\text{Ra}$ and $[228/226]$ as a function of salinity in the surface waters of the western Bay of Bengal	34
3.8	Plots showing $^{228}\text{Ra}$ versus distance from the coast along the six coast-to-open ocean tracks	37
3.9	Contour maps of the distribution of measured and model-derived surface $^{228}\text{Ra}$ concentration of the Bay of Bengal	41
3.10	Contour maps of the distribution of measured and model-derived surface $^{226}\text{Ra}$ concentration of the Bay of Bengal	42
3.11	3-D plots of K versus $w_x$ and $w_y$ .	47
3.12	$^{226}\text{Ra}$ water column profiles of the Bay of Bengal	49
3.13	$^{226}\text{Ra}$ water column profiles of the Arabian Sea	50
5.1	Map showing the Yamuna and the Chambal rivers	79
5.2	Geological lithologies of the Yamuna river catchment	80
5.3	Mean monthly temperature and rainfall variations at the Yamuna catchment.	82
5.4	Mean monthly variation of the water discharge in the Yamuna	83
5.5	Geological lithologies of the Chambal river catchment	87
5.6	Mean monthly variations of maximum, minimum temperatures and rainfall in the Chambal catchment.	89
5.7	Mean seasonal water discharge in the Chambal river	90

5.8	Sampling location of the Chambal river basin	93
5.9	Sampling location of the Yamuna river basin	94
5.10	Analytical scheme for analysis of sediment and water samples	98
5.11	Analytical scheme for separation of REE using cation exchange resin from sediments for ICPAES technique	99
5.12	(a) Repeat measurements of REE of G-2 plotted against each other and (b) comparison of measured and reported REE concentrations in the reference standards.	100
5.13	Comparison of concentrations of REE in the Yamuna bed sediment samples measured by ICPAES and INAA techniques	104
6.1	Distribution of total dissolved solids (TDS) in the Chambal river	113
6.2	Plot of conductance against TDS in the Chambal river water samples	114
6.3	Plot of $TZ^+$ against $TZ^-$ in the Chambal river	118
6.4	Scatter plots showing relationships between major solutes in the Chambal river water samples	119
6.5	Plot of $HCO_3$ against total anions in the Chambal river water samples	120
6.6	Ternary plots of major cations and anion compositions ( $\mu Eq$ ) for the river waters of the Chambal catchment	122
6.7	River flow diagram showing $HCO_3$ and Ca/Mg molar ratio variations downstream of the Chambal river	123
6.8	Scatter plot of Mg concentration and Ca/Mg molar ratio against Ca concentration in the Chambal river waters and histogram of calcite saturation index (CSI) distribution	124
6.9	Cross-plot of Cl and Na with line indicating relative proportions in marine aerosols	125
6.10	Correlation Plots of $NO_3$ against $SO_4$ and Cl against $SO_4$ in the Chambal river waters	126
6.11	(a) $HCO_3$ vs. $(Na^+ + K)$ , (b) $Mg/Na^+$ vs. $Ca/Na^+$ and (c) Si vs $(Na^+ + K)$ in the Chambal river waters	127
6.12	TDS vs $\Sigma REE$ (b) TDS vs. La in the Yamuna river water	137
6.13	Dissolved REE concentrations normalized to that of PAAS for the Yamuna river water samples	144
6.14	Distribution of pattern of REE normalized to PAAS in river waters and sediments of the Yamuna river	146
6.15	Histogram of the Shale normalized Eu and Ce anomalies in the Yamuna river water samples	146
6.16	Scatter plot of PAAS normalized concentrations of Yb vs Nd	147
6.17	Histogram of the Shale normalized Gd anomalies ( $Gd/Gd^*$ ) in the Yamuna river water samples	148
6.18	Triangular $Al_2O_3 - (CaO + Na_2O) - K_2O$ plot of sediment samples of Yamuna, Chambal and Ganga rivers	153
6.19	Triangular $Al_2O_3 - CaO + Na_2O + K_2O - (Fe_2O_3 + MgO)$ plot of sediment samples	154
6.20	Variation of CaO, MgO, $P_2O_5$ , $Fe_2O_3$ , Ti and Mn with $Al_2O_3$ in bed sediments of the Chambal river	155
6.21	Distribution of Ce and Eu anomalies in bed sediments of the	166

	Yamuna and the Chambal rivers	
6.22	PAAS normalized REE composition of the Deccan basalts and the Chambal river sediments	167
6.23	PAAS normalized REE composition of the granites and bed sediments of the Yamuna river	168
6.24	PAAS normalized REE composition of the granites and bed sediments of the Yamuna tributaries	169
6.25	PAAS normalized REE composition of the bed sediments of the Ganga river and its tributaries	170
6.26	Distribution pattern of REE normalized to PAAS of the Yamuna and the Chambal rivers	171
6.27	Scatter plots of Ce vs Fe and Ce vs Mn for the bedload sediments of the Chambal and the Yamuna catchments	172
6.28	Variations in (a) $\text{Al}_2\text{O}_3$ vs $\Sigma\text{REE}$ (b) $\text{P}_2\text{O}_5$ vs $\Sigma\text{REE}$ (c) $\text{Al}_2\text{O}_3$ vs La (d) $\text{Al}_2\text{O}_3$ vs Yb (e) CaO vs $(\text{La/Yb})_{\text{CN}}$ and (f) $\text{Al}_2\text{O}_3$ vs $(\text{La/Yb})_{\text{CN}}$ .	173
6.29	Plot of La against P in the bed sediment samples of the Chambal and the Yamuna rivers	174
6.30	Variation of Eu against Sm of the bed sediments of the Chambal and Yamuna rivers	175
6.31	Plot of Ce/Eu against Eu/Sm of the bed sediments of the Yamuna and Chambal rivers	176
6.32	UCC-normalize multi-element diagram of the Chambal and the Yamuna sediments	177
6.33	Elemental enrichment factors of the Chambal and the Yamuna river sediments	179
7.1	Distribution of dissolved uranium in the Yamuna and Chambal rivers	193
7.2	Plot of dissolved uranium concentration against $\Sigma\text{cat}^*$	196
7.3	Variations of uranium concentration against $\text{HCO}_3$	197
7.4	Variation of $\Sigma\text{cat}^*$ and $\text{HCO}_3$ in the Yamuna and the Chambal rivers.	198
7.5	Correlation plot of dissolved uranium versus Cl	198
7.6	U/Na* weight ratios in the Chambal and the Yamuna rivers	202
7.7	Plot showing (a) and (b) Re versus U in the Yamuna mainstream and tributaries, (c) $^{234}\text{U}/^{238}\text{U}$ activity ratio versus $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio and (d) $^{234}\text{U}/^{238}\text{U}$ activity ratio versus $\text{HCO}_3$ of the Yamuna river water samples.	205
7.8	Histograms showing dissolved $^{234}\text{U}/^{238}\text{U}$ activity ratio	207
7.9	Plot of $^{234}\text{U}/^{238}\text{U}$ activity ratio versus reciprocal uranium concentration	208
7.10	River flow diagram of uranium of the Chambal river	209
7.11	River flow diagram of uranium of the Yamuna river	210



For Fulltext Please Contact  
To

[rajan@prl.res.in](mailto:rajan@prl.res.in)