Geochemical and Isotopic studies of Waters and sediments of Arabian and Andaman Seas

A THESIS

Submitted for the Award of Ph.D. degree of

MOHANLAL SUKHADIA UNIVERSITY

In the

Faculty of Science

by

Damodararao Karri



Under the Supervision of

Dr. Sunil Kumar Singh PROFESSOR PHYSICAL RESEARCH LABORATORY, AHMEDABAD

DEPARTMENT OF GEOLOGY MOHANLAL SUKHADIA UNIVERSITY, UDAIPUR

2016

DECLARATION

I, Mr. Damodararao Karri, S/o Mr. Polayya, resident of J-117, PRL residences, Navrangpura, Ahmedabad – 380009, hereby declare that the research work incorporated in the present thesis entitled "Geochemical and Isotopic studies of Waters and sediments of Arabian and Andaman Seas" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required.

I solely own the responsibility for the originality of the entire content.

Date:

(Damodararao Karri)

CERTIFICATE

I feel great pleasure in certifying that the thesis entitled "Geochemical and Isotopic studies of Waters and sediments of Arabian and Andaman Seas" embodies a record of the results of investigations carried out by Damodararao Karri under my guidance.

He has completed the following requirements as per Ph.D. regulations of the University

- (a) Course work as per the university rules
- (b) Residential requirements of the university
- (c) Presented his work in the departmental committee

(d) Published/accepted minimum of one research paper in a referred research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

I recommend the submission of thesis.

Date:

Name and designation of supervisor Sunil Kumar Singh, Professor

Countersigned by

Head of the Department

Dedicated To My Parents, Smt. Ramulu & Sri. Polayya With this thesis work I contribute my drop to the field of oceanography. I have several people to thank for their sincere help, support and guidance.

First of all, I am sincerely grateful to my supervisor, Prof. Sunil K. Singh, who introduced me to the world of marine biogeochemistry and fluvial geochemistry. His deep insight and expertise in isotope geochemistry and mass spectrometry helped to build a strong foundation for this work. It was a great experience to work with him during field trips, experimental analyses, exploring every aspect of science. I appreciate his friendly and kind hearted nature which encouraged me to have fruitful scientific discussions with him. I acknowledge him for his continuous support and guidance. He gave me enough freedom to venture into various aspects of my research work.

I also express my deep gratitude to late Prof. S. Krishnaswami (Swami) for his valuable suggestions and views during this work. It was an honor to work with such a great geochemist. I am also thankful to him for his valuable comments and suggestions. I sincerely thank Prof. M. M. Sarin for his support and suggestions during my thesis work and for his great guidance during my course work project. He instilled in me the discipline of handling scientific instruments and streamlining a research objective.

I am grateful to Dr. V. K. Rai for his valuable help during the measurements of various isotope systematics using MC-ICP-MS. He made me at ease with the operation and working of the MC-ICP-MS.

I am enormously thankful to the PRL Director and the Dean for providing me support and facilities throughout the thesis work. I thank academic committee members for timely evaluation of my research work. Special thanks to Profs. R. Ramesh, J. S. Ray, S. Ramachandran, Drs. L. K. Sahu, V. K. Rai, R. Rangarajan, K. K. Marhas, S. Kumar, V. Sheel, B. K. Sahu, J. R. Bhatt, D. Chakrabarty, for their instructive lectures during course work. My special thanks to Drs. Ravi Bhushan, Neeraj Rastogi and R. Rengarajan for their fruitful suggestions and comments to improve my thesis quality. I am grateful to Drs. Vineet Goswami and Jayati Chatterjee for their help in the inverse model calculations and experimental work throughout this period.

I would like to thank all Chemistry Lab members for their tremendous help and encouragement during my thesis work. First of all, I would like to thank Bhavsar bhai for helping me throughout the thesis work. It was a great experience working with him in the lab as well as on oceanographic expeditions. I thank Mr. Sudheer, for their help and guidance during this research work. I sincerely thank my lab-mates Sneha, Upasana, Subha, Ravikant, Balaji, Priyanka, Abhishek, Anil, Mahesh, Naman, Chinmay, Harsh Raj, Romi, Sanjukta, Akshay, Ankur and Sajid for their help and moral support. I thank my seniors Gyana, Rahaman, Prashant, Satinder, Kirpa, Ashwini, Timmy, Alok, Neeraj, Arvind, Amzad and Rubi for their valuable suggestions.

I would also like to thank my previous lab-associates Rupali, Batuk, Nitesh, Preksha, Utsav, Nikita, Dipjyoti, Jivesh, Wriju, Aswathy and Prabhuti for being part of the Chemistry lab family. I appreciate Sneha, Trupti, Vaishali, Jaldhi, Ramsha, Pravin, Rashmit and Shantaben for helping me with the administrative procedures.

I duly thank to all GSDN members for their help and support during this work. I want to especially thank Mr. Manan Shah and Mr. Lakan Singh for their expertise on the functioning of instruments and timely solving the problems associated with them.

I am grateful to all the staff members of Library, Computer Centre, Workshop, Administration, Purchase, Dispensary, and Maintenance section of PRL for their assistance and cooperation.

I owe my sincere thanks to Department of Space (DOS) for the scholarship and support for the research. My sincere thanks to Dr. V. Ramaswamy and P. S. Rao for providing sediment samples from the Andaman Shelf. I thank to MoES, Government of India for financial and logistic supports provided to GEOTRACES (India) programme. My thesis is part of this programme. I thank NCAOR and NORINCO for resourceful help during the ocean expeditions. I Thank to Mr. M. M. Subramaniam for his help and support during ocean expedition. I thank the captains, crew and scientific members of FORV Sagar Sampada cruise No. 300, Saga Kanya cruise No. 304 and Sagar Manjusha 13/24 and 13/29. I thank Goldschmidt committee for providing funds for conferences held in Prague, Czech Republic and Yokahama, Japan.

I take this opportunity to express gratitude to all my friends at PRL. I would like to thank my batchmates of JRF10: Aathi, Anjali, Arko, Ashok, Avadhesh, Bhavya, Dilip, Dinesh, Debasis, Gangi, Gaurav, Gaurav S, Girish, Gulab, Kalyan, Lata, Lekshmy, Midhun, Monojit, Naveen, Nigam, Priyanka, Tanmoy, Uma, Upendra, Vinay, Wageesh and Yashpal. I give my Special thanks to Anirban, Abhaya, Arvind, Bivin, Deepak, Gulshan, Harsh, Fazlul, Shasi, Yogita, Jinia, Manab, Nita, Sowmya, Shrema, Kuldeep, Vijay, Jinia, Manu, Rupa, Niharika, Sneha, Saweeta, Shraddha and Ikshu for a very nice company during my stay at hostel. I thank Lathika, Racheal, Manoj, Vissu, Mangalaa, Sagar and Kalpana for their support during my research. I thank all Telugu friends Krishna Veni, Deepthi, Chandana, D. P. Karanam, Suneel, Srinivas, Gangi, Aditya, Aslam, Venky, Satish, Kiran, Sameer, Ejaz, Prasad, Jaya Krishna, Malai and Sekhar for their help and support throughout my work.

I sincerely thank Mrs. Renu Singh and Markandeya for making me feel like part of their family. I thank Dimple and Sharada for their care, and of course for the delicious food.

Finally, I would like to acknowledge my parents, brothers, and in-laws for showing believing in me and encouraging me to explore the fields of science. I thank to my niece Manasa and nephews Prudhvi, Balu, and Mokshagna.

	List of abbreviations and symbols
AABW	: Antarctica bottom waters
AAIW	: Antarctic Intermediate Waters
ACC	: Antarctic Circumpolar Current
AS	: Arabian Sea
ASHSW	: Arabian Sea high saline surface waters
BoB	: Bay of Bengal
BoBSW	: Bay of Bengal surface waters
BRMN	: Brahmani
CCR	: CO ₂ consumption rates
CDW	: Circumpolar Deep Water
CER	: Carbonate erosion rate
CGGC	: Chotanagpur Granite Gneiss complex
CV	: Coefficient of Variation
CHUR	: Chondritic Uniform Reservoir
CIA	: Chemical index of alteration
CSI	: Calcite Saturation Index
CTD	: Conductivity-Temperature-Density
DEM	: Digital Elevation Map
DO	: Dissolved Oxygen
EGMB	: Eastern Ghats Mobile Belt
EICC	: East India Coastal Current
EIGB	: East Indian Ghats belt
EJ	: Equatorial Jet
F-AAS	: Flame-Atomic absorption spectroscopy
G-B	: Ganga-Brahmaputra
GDV	: Godavari
GRS	: Godavari River System
HH	: Higher Himalaya
HREEs	: Higher Rare Earth Elements
IBA	: Indo–Burman–Arakan
IC	: Ion chromatography
ICP-AES	: Inductively coupled plasma atomic emission spectroscopy
ID	: Isotope dilution
IIW	: Indonesian Through Flow Intermediate Water
IOG	: Iron Ore group
ITF	: Indonesian Through Flow
IW	: Indonesian Through Flow surface Water
JMC 321	: Neodymium isotope standard solution
JMC 475	: Hafnium isotope standard solution
KR	: Krishna River
L	: Litter

LH	: Lower Himalaya
LREEs	: Lower Rare Earth Elements
Ma	: Million annum
MC-ICP-MS	: Multicollector Inductively Coupled Plasma Mass Spectrometer
MND	: Mahanadi
MQ	: Milli-Q water
MT	: Million tons
NADW	: North Atlantic deep waters
NASC	: North American Shale Composite
NE	: North-East
NICB	: Normalized inorganic charge balance
NIDW	: North Indian Deep Water
NIIW	: North Indian Intermediate Water
OMG	: Older Metamorphic Group
OMZ	: Oxygen minimum zone
ORNL	: Oak Ridge National Laboratory
ORV	: Ocean Research Vessel
PAAS	: Post Archean Australian Shale
PGW	: Persian Gulf waters
рр	: Poly Propylene
PRL	: Physical Research Laboratory
PTFE	: Poly tetrafluoroethylene
QD	: Quartz distilled
Q-ICM-MS	: Quadrupole Inductively Coupled Plasma Mass Spectrometer
REE	: Rare Earth Elements
RSD	: Relative standard deviation
RSW	: Red Sea waters
RTB	: Rajahmundry Traps Basin
SER	: Silicate erosion rate
SGD	: Submarine groundwater discharge
SIS	: Stable Introduction System
SK	: Sagar Kanya
SLRS-4	: Canadian River water standard
SM	: Sagar Manjusha
SPM	: Suspended particulate matters
SRM 987	: Strontium Carbonate Isotopic Standard
SS	: Sagar Sampada
SW	: South-West
TD	: Teflon distilled
TDS	: Total dissolved solids
TEIs	: Trace elements and isotopes
TML	: Theoretical mixing line
UC	: Upper crust
θ -S- σ_{θ}	: Temperature, salinity and potential density
α	: Alpha

β	: Beta
δ	: Delta
μ	: Micro
3	: Epsilon
σ	: Sigma
θ	: Theta

ABSTRACT

Distribution of trace elements in the ocean regulates productivity, ecosystem dynamics, carbon cycle and hence the global change. This thesis work attempts to identify and quantify the sources and sinks of selected trace elements by studying them in riverine-estuarine system, in the shelf region and in the open Indian Ocean. Erosion and weathering in the Peninsular Indian Rivers, the Godavari, the Mahanadi and the Brahmani basins seems to be controlled dominantly by lithology and runoff. Annually, they supply 25 MT of total dissolved solids, 150 Mmol of Sr and 12 thousands moles of Nd to their respective estuaries and sequester ~1% of atmospheric CO₂ through silicate weathering, similar to their drainage area proportion. Riverine fluxes get modified significantly in the estuaries before reaching to the open ocean. Release/desorption from the Fe-Mn oxy-hydroxide coating of the continental sediments found to be the potential source of dissolved rare earth elements (REE) and Mn in the East Indian estuaries and supply ~260 Mg of dissolved Nd annually to the Bay of Bengal, quite significant to the missing Nd in its global budget. This study identified submarine groundwater discharge (SGD) as an important source of dissolved Sr to East Indian estuaries. The annual Sr flux through the SGD from East Indian estuaries is 780 Mmol ~3-11% of the global SGD Sr flux and could be very important for the global Sr budget. This study, for the first time, recognized the higher erosion on the western slopes of the granitic ranges of the Southern Myanmar, supplying a significant amount of sediment to the Eastern Andaman Shelf in addition to the Indo-Burman Ranges. Runoff and relief control erosion and weathering in the hinterland of the Irrawaddy, Salween and western Myanmar basins. Further, this study quantified the different water masses present in the Arabian Sea using dissolved ε_{Nd} and ε_{Hf} . Bottom and deep waters of the Arabian Sea are dominated by the Antarctic Bottom Waters (50-85%) and the North Atlantic Deep Waters (25-60%). The Red Sea Waters (25-80%) and the Persian Gulf Waters (5-17%) occupy the intermediate depth. Surface waters of the Arabian Sea are composed of the Arabian Sea High Salinity Waters (40-85%) and the Bay of Bengal (20-50%). Atmospheric dust is found to be an important source of dissolved Nd to the surface waters of the Central Arabian Sea whereas sediments from the Indus Rivers deliver less radiogenic Nd to the Northern Arabian Sea waters.

CONTENTS

Pages

List of Tablesvi				
List	of Figu	res	ix	
Chapter 1	hapter 1 Introduction			
- · · I · · ·	1.1	Introd	uction2	
	1.2	Object	tives of the thesis15	
	1.3	Study	area15	
	1.4	Struct	ure of the thesis16	
Chanter 2	Mata	rials an	d Methods 19-87	
Chapter 2	21	Study	area 20	
	4.1	2 1 1	Godavari River System 21	
		2.1.1 2 1 2	Mahanadi and Brahmani Piyer Systems 23	
		2.1.2 2 1 3	Fast Indian Estuarias	
		2.1.3 2 1 1	Andomon Shalf Pasin 27	
		2.1.4	Arabian Saa and Indian Ocean 30	
	22	2.1.3 Geolo	Arabian Sea and mutan Ocean	
	2.2	221	Godavari Piver Basin 37	
		2.2.1	2 2 1 1 The Decean Trans 32	
			2.2.1.1 The Decean Traps	
			2.2.1.2 Rajannunury Traps Dasin	
			2.2.1.5 Archean Enhologies	
			rocks 34	
		222	The Mahanadi and Brahmani River	
		2.2.2	hasing geology 34	
			2 2 2 1 Granite Graissic complex of Chotanagnur	
			torrain 35	
			2222 Precambrian Rocks of Singhbhum and	
			Bastar craton 35	
			2 2 2 3 Gondwana Bocks 38	
		2.2.3	The N-E Andaman catchment basin geology38	
	2.3	Field S	Sampling42	
		2.3.1	The Arabian Sea and Indian Ocean waters42	
		2.3.2	River, estuary and rain water samples43	
		2.3.3	Sediment samples53	
			2.3.3.1 Sediment samples from the Andaman Shelf	
			region and Irrawaddy River Basin54	
			2.3.3.2 Sediment samples from the Godavari River	
			basins54	
			2.3.3.3 Suspended Particulate Matters (SPM)54	
	2.4	Analy	tical Methods54	
		2		

{ i }

		2.4.1	Sample	collection and onboard procedures for
			Hf in wa	ater samples
			2.4.1.1	Procedures for Hf separation and
				measurement of its isotope
				composition
			2.4.1.2	Hf concentration measurements in
				seawaters using isotope
				dilution method
			2.4.1.3	Preparation and Calibration
				of Hf spike
		2.4.2	Samples	collection and onboard
			pre-conc	centration procedures for Nd isotopes
			and its c	oncentration in water samples66
			2.4.2.1 H	Procedures for Nd isotopes measurement in
				the seawater samples67
			2.4.2.2	REE's concentration measurements using
				isotope dilution method71
			2.4.2.3	Preparation and calibration of
				REE spikes72
		2.4.3	River an	ad estuary waters chemistry76
			2.4.3.1	Procedures for Sr-Nd isotope
				measurements in the river and
				estuarine waters76
			2.4.3.2	Trace elements analysis in river and
				estuarine waters78
			2.4.3.3	Major ions and silicate measurements in
			a 1'	river and estuary waters80
		2.4.4	Sedimer	nts80
			2.4.4.1 H	Powdering
			2.4.4.2	Jeochemical and isotopic Analysis85
			2.4.4.3 3	SF-ING ISOTOPES ANALYSIS
			2.4.4.4 ľ	viajor Elements chemistry
Chaptor 3	Frosio	n and V	Woothor	ing in the Peningular Indian Divers
Chapter 5	and flu	ives to 1	the Ray	of Rengal 88-141
	31	Introdu	iction	89
	3.2	Results	<u>.</u>	
	0.2	3.2.1	The dis	solved chemical composition in the
		01211	penins	lar Indian River systems
		3.2.2	Primary	v observations in the peninsular Indian
		-	River s	vstems
	3.3	Discus	sions	
	`	3.3.1	Spatial	and inter-annual variations in major ions.
			TDS	
		3.3.2	Spatial	and inter-annual variation in Sr
			concent	trations and ⁸⁷ Sr/ ⁸⁶ Sr ratios109

-{ " }

		3.3.3	Sources of Major ions and Sr in the peninsular
			Indian Rivers111
		3.3.4	Inverse Modeling113
			3.3.4.1 <i>a priori</i> values of end-members 114
			3.3.4. 2 <i>a posteriori</i> values 115
		335	Forward modeling in the Mahanadi and the
		5.5.5	Brahmani basing 115
		226	Chamical woothering rotes 118
		3.3.0	Chemical weathering fates
			3.3.0.1 Sincate erosion rate
			3.3.6.2 Carbonate erosion rate120
			3.3.6.3 CO ₂ consumption rate
		3.3.7	⁵ /Sr/ ⁶⁶ Sr as a proxy of silicate weathering
			in the peninsular rivers124
		3.3.8	Sources of dissolved Sr in the peninsular Indian
			Rivers126
		3.3.9	Dissolved rare earth elements in the peninsular
			Indian rivers and ε_{Nd} Behaviour in the GRS129
		3.3.10	Neodymium isotope composition in the GRS132
		3.3.11	The particulate chemical composition
			in the GRS 134
		3.3.12	Provenance study using Sr and Nd Isotopic
		0.0.12	systematics 136
	3.4	Conclu	usions139
Chapter 4	3.4 Behav East I	Concle viour of Indian I	Trace Elements and Isotopes in the Estuaries: Implications to Their
Chapter 4	3.4 Behav East I Globa	Concle viour of Indian I I Marin	Isions
Chapter 4	3.4 Behav East I Globa 4.1	Conclu viour of Indian I Il Marin Introd	Trace Elements and Isotopes in the Estuaries: Implications to Their ne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I Il Marin Introd Result	usions
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I Introdu Result 4.2.1	Isions
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu ziour of Indian I Introdu Result 4.2.1 4.2.2	Isions 139 Trace Elements and Isotopes in the Estuaries: Implications to Their ne Budget 142-186 action 143 s 146 Dissolved Sr and ⁸⁷ Sr/ ⁸⁶ Sr. 147 Major ions in estuarine waters 149
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3	usions
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget.142-186action.143s.146Dissolved Sr and 87 Sr/ 86 Sr.147Major ions in estuarine waters.149REEs and ε_{Nd} Behaviour in East Indianestuarine waters.149
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Concluzion of Cindian I Introdu Introdu Result 4.2.1 4.2.2 4.2.3	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of indian I il Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget.142-186action.143s146Dissolved Sr and 87 Sr/ 86 Sr.147Major ions in estuarine waters.149REEs and ε_{Nd} Behaviour in East Indianestuarine waters.149 87 Sr/ 86 Sr, ε_{Nd} , and concentration of majorelements, Sr and Nd in sediments.157pH, dissolved Oxygen and dissolved Mn in EastIndian Estuaries159
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discuss	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of indian I il Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget.142-186action.143s146Dissolved Sr and 87 Sr/ 86 Sr.147Major ions in estuarine waters.149REEs and ε_{Nd} Behaviour in East Indianestuarine waters.149 87 Sr/ 86 Sr, ε_{Nd} , and concentration of majorelements, Sr and Nd in sediments.157pH, dissolved Oxygen and dissolved Mn in EastIndian Estuaries.159ssion.161Behaviour of dissolved Sr and 87 Sr/ 86 Sr in
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget.142-186action.143s146Dissolved Sr and 87 Sr/ 86 Sr.147Major ions in estuarine waters.149REEs and ε_{Nd} Behaviour in East Indianestuarine waters.149 87 Sr/ 86 Sr, ε_{Nd} , and concentration of majorelements, Sr and Nd in sediments.157pH, dissolved Oxygen and dissolved Mn in EastIndian Estuaries.159ssion.161Behaviour of dissolved Sr and 87 Sr/ 86 Sr inmixing zone and their applications to SGD
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of indian I Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget.142-186action.143s146Dissolved Sr and 87 Sr/ 86 Sr.147Major ions in estuarine waters.149REEs and ε_{Nd} Behaviour in East Indianestuarine waters.149 87 Sr/ 86 Sr, ε_{Nd} , and concentration of majorelements, Sr and Nd in sediments.157pH, dissolved Oxygen and dissolved Mn in EastIndian Estuaries.159ssion.161Behaviour of dissolved Sr and 87 Sr/ 86 Sr inmixing zone and their applications to SGD.1614.3.1.1Behaviour of dissolved Sr concentration
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of Indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in the Estuaries: Implications to Their ne Budget.142-186 action.143s146Dissolved Sr and 87 Sr/ 86 Sr.147Major ions in estuarine waters.149REEs and ε_{Nd} Behaviour in East Indian estuarine waters.149 87 Sr/ 86 Sr, ε_{Nd} , and concentration of major elements, Sr and Nd in sediments.157pH, dissolved Oxygen and dissolved Mn in East Indian Estuaries.159ssion.161Behaviour of dissolved Sr and 87 Sr/ 86 Sr in mixing zone and their applications to SGD.1614.3.1.1 Behaviour of dissolved Sr concentration in the East Indian estuaries.
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in the Estuaries: Implications to Their ne Budget.142-186 action.143145146Dissolved Sr and 87 Sr/ 86 Sr.147Major ions in estuarine waters.149REEs and ε_{Nd} Behaviour in East Indian estuarine waters.149 87 Sr/ 86 Sr, ε_{Nd} , and concentration of major elements, Sr and Nd in sediments.157pH, dissolved Oxygen and dissolved Mn in East Indian Estuaries.159Sion.161Behaviour of dissolved Sr and 87 Sr/ 86 Sr in mixing zone and their applications to SGD.1614.3.1.1 Behaviour of dissolved Sr concentration in the East Indian estuaries.1614.3.1.2 Behaviour of dissolved Sr concentration in the East Indian estuaries.
Chapter 4	3.4 Behav East I Globa 4.1 4.2 4.3	Conclu viour of indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of indian I il Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2	Conclu viour of indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget
Chapter 4	3.4 Behav East I Globa 4.1 4.2 4.3	Conclu viour of indian I I Marin Introdu Result 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 Discus 4.3.1	139Trace Elements and Isotopes in theEstuaries: Implications to Theirne Budget.142-186action 143action 143s.142-186dist colspan="2">action 142-186action 143s.142-186action 143s.143s.146Dissolved Sr and ⁸⁷ Sr/ ⁸⁶ Sr.147Major ions in estuarine waters149REEs and ε_{Nd} Behaviour in East Indianestuarine waters14987 Sr/ ⁸⁶ Sr, ε_{Nd} , and concentration of majorelements, Sr and Nd in sediments157pH, dissolved Oxygen and dissolved Mn in EastIndian Estuaries1614.3.1.1 Behaviour of dissolved Sr and ⁸⁷ Sr/ ⁸⁶ Sr inmixing zone and their applications to SGD1614.3.1.2 Behaviour of dissolved ⁸⁷ Sr/ ⁸⁶ Sr in mixing zone20164.3.1.3 Characterizing SGD and estimate of SGD fluxes in estuaries using

_____(iii)_____

			inverse modeling165
			4.3.1.4 SGD flux of Sr from the East
			Indian estuaries to the Bay of Bengal171
		4.3.2	Behaviour of geochemical elements,
			Sr and ⁸⁷ Sr/ ⁸⁶ Sr in SPM175
		4.3.3	Behaviour of the dissolved REEs and ε_{Nd}
			in mixing zone177
	4.4	Implic	ations184
	4.5	Summ	ary and conclusions185
Chapter 5	Lithol	ogy, m	onsoon and sea-surface current control
	on pro	ovenan	ce, dispersal and deposition of sediments
	over t	he And	aman continental shelf187-208
	5.1	Introd	uction188
	5.2	The al	oundances of major elements, Sr and Nd and
		Sr-Nd	isotope compositions in the Andaman
		Shelf	basin189
		5.2.1	Major Element Compositions and Implications for
			Provenance193
		5.2.2	Provenance Tracing Using Sr and Nd Isotopic
			Systematics196
		5.2.3	Control on Erosion Determining the Sediment
		5 3 4	Sources
		5.2.4	Role of Sea-Surface Current in Controlling the
	5 2	Canal	Sediment Dispersion
	5.5	Conci	usions
Chapter 6	Dissol	ved Hf	and Nd concentration and their
	isotop	ic comj	positions in the Indian Ocean:
	Implic	cations	to water-particles interaction,
	upwel	ling, w	ater mass mixing and their sources209-256
	6.1	Introd	uction210
		6.1.1	Evolution of Hafnium and neodymium
			isotopes212
		6.1.2	Hydrology of the Indian Ocean214
		6.1.3	North-East and Southern Indian Ocean
			water masses215
		6.1.4	The Arabian Sea water masses218
	6.2	Result	s and discussions220
		6.2.1	Dissolved Nd concentrations in the Arabian
			Sea: Their sources and input mechanism225
		6.2.2	Nd isotopic compositions in
			the Arabian Sea waters231
		6.2.3	Quantification of the Arabian Sea water
			masses: inverse modeling approach232
		6.2.4	<i>a priori</i> values of the end members

(iv)

			(source water masses)	235
		6.2.5	<i>a posterior</i> values of the end members	
			(source water masses)	235
		6.2.6	The Arabian Sea water masses	236
		6.2.7	Estimates of Nd budget, Nd ^{excess} and	
			their ε_{Nd} {(ε_{Nd}) ^{excess} } from the inverse mode	el240
		6.2.8	Hf concentrations and isotopic	
			compositions in the Indian Ocean	243
			6.2.8.1 Concentrations of dissolved Hf in	
			the Indian Ocean	243
			6.2.8.2 Hf isotopic compositions in	
			the Indian Ocean water masses	250
	6.3	Concl	usions	255
Chapter 7	Cone	lusions	and future perspectives	.257-265
	7.1	Chem	ical erosion in the Peninsular Indian	
		rivers	and associated chemical fluxes to	
		the Ba	ay of Bengal	258
	7.2	Behav	viour of trace elements and isotopes in solute	
		and pa	articles of the Eastern Indian Estuaries:	
		Implic	cations to their global marine budget	
	7.3	Lithol	ogy, monsoon and sea surface current	
		contro	ol on provenance, dispersal and	
		depos	ition of sediments over the Andaman	
		contin	ental shelf	
	7.4	Disso	lved ε_{Nd} and ε_{Hf} in the Indian Ocean	
		waters	s: Implications to water-particle	
		intera	ction, upwelling, water mass mixing and	
		their s	ources	262
	7.5	Future	e perspectives	
References				269-313
I ist of much	antion			21/ 216
List of public	cations	Š		

LIST OF TABLES

Table	Contents	Page
2.1	The Physical properties of the peninsular Indian Rivers	24
2.2	Details of sampling for seawater in the Arabian Sea	44
2.3	Details of sampling for seawater in the Indian Ocean	45
2.4	Details of sampling for surface sediments of the Andaman Shelf basin	45
2.5	Water and sediment sampling details of the Godavari River System	47
2.6	Water and sediment sampling details of the Mahanadi and Brahmani Rivers	48
2.7	Details of sampling for water and SPM in East Indian estuaries	49
2.8	Reagents used for the chemical processing of the samples collect during this study	55
2.9	Purification of Hf isotopes from seawaters using three column chemistry	59
2.10	The parameters of MC-ICPMS during Sr-Nd-Hf isotopes measurements	61
2.11	Atomic abundances of Hf isotopes in the natural sample and the spike	64
2.12	Results of calibrated Hf Spike	64
2.13	Hf purification on Nobias chelate PA1 resin	65
2.14	The precision of concentrations of Hf in seawater	66
2.15	Purification of Nd isotopes from natural waters using three column chemistry	68
2.16	The basic details of REE spikes procured from ORNL	72
2.17	The REEs isotopes, abundances, isotope ratios and atomic weights of natural and spike solutions	73
2.18	Calibrated concentrations in mixed REE Spike	73
2.19	REE's purification on Nobias-Chelate PA1 resin	74
2.20	The precision of Sr concentration and its isotopic compositions in this study	79
2.21	The precision of concentration of REEs in this study	81
2.22	The accuracy and precision of major ions, Si and Mn of standard and natural waters	82
2.23	The precision of concentration of major ions of natural waters in this study	83
2.24	The precision of Sr-Nd concentration and their isotopes in sediments	84
2.25	The precision of concentration of major elements in sediments	86

3.1	Dissolved chemical composition and Sr-Nd isotopic	94
	Concentration of REEs in the Godavari, and the Mahanadi	~-
3.2	Rivers waters	97
3.3	Major elements, Sr and Nd abundances and Sr-Nd isotopic compositions in the particulates of the GRS	99
3.4	<i>a priori</i> molar ratio for the various end members and associated uncertainties in the Godavari River system	116
3.5	<i>a posteriori</i> values of various end members contributing to the GRS, obtained from the inverse model	116
3.6	<i>a priori</i> molar ratio for the various end members and associated uncertainties in the Mahanadi and the Brahmani Rivers	117
3.7	The SER, CER, Sr fluxes and CCR by chemical weathering for the streams	122
3.8	The comparison of SER, CER and CCR of the peninsular Indian Rivers with Global major rivers	124
3.9	Indian Rivers to the Bay of Bengal	129
4.1	The Physical properties of the Ganga, Mahanadi, Krishna and the Godavari Rivers	147
4.2	Concentration of Sr and ⁸⁷ Sr/ ⁸⁶ Sr ratio in East Indian estuaries	148
4.3	Major ion composition in East Indian estuarine waters	151
4.4	Dissolved Mn, REEs abundances and isotope composition of Nd in East Indian estuaries	153
4.5	The amount of SPM, particulate Sr-Nd concentrations and their isotope compositions in East Indian estuaries	160
4.6	<i>a priori</i> data of Salinity, Sr and ⁶⁷ Sr/ ⁶⁶ Sr of various sources in East Indian estuaries	167
4.7	<i>a posteriori</i> values of SGD contributing salinity, Sr and "Sr/"Sr in East Indian estuaries	167
4.8	gradient in East Indian estuaries The SGD flux and Sr flux through SGD along with their errors in	172
4.9	East Indian estuaries	173
5.1	The major elements, Sr and Nd abundances and Sr-Nd isotope ratios in the Andaman Shelf sediments	191
5.2	The end members with their isotopic properties of various sources of Northern Andaman Shelf sediments	200
6.1	Salinity, potential temperature, concentration of Nd and their isotope compositions in the Arabian Sea waters	220
6.2	<i>a priori</i> and <i>a posterior</i> values of various water masses end members used in the inverse model computations	234

6.3	Excess Nd and their ε_{Nd} in the Arabian Seawaters computed using the inverse modeling of the data	239
6.4	Salinity, potential temperature, concentration of Hf and its isotope composition in the Indian Ocean waters	244

Flow chart

2.1	The field samples and the measured chemical compositions	41
2.2	The methodology for seawater samples analysis	56

LIST OF FIGURES

Figure	Contents	Page
1.1	The possible sources of trace elements and isotope to the ocean basin	4
1.2	The generalized modern global ocean circulations.	11
2.1	The overview map of the study areas covered in this thesis	21
2.2	The sampling location map of the Godavari River system	22
2.3	The sampling location map of the Mahanadi and the Brahmani Rivers systems	25
2.4	The sampling location map of the East Indian estuaries	26
2.5	The sampling location map of the northern Andaman Sea	28
2.6	The sampling location map of the Arabian Sea	31
2.7	The geological map of the Godavari River system	33
2.8	The geological map of the Mahanadi and Brahmani Rivers	37
2.9	The lithology map of the drainages of the Myanmar and Southern Thailand	39
2.10	Collection and processing of natural water and sediment samples	51
2.11	The purification of Hf using Ln-Spec resin from seawaters fractions	60
2.12	Measurement of ¹⁷⁶ Hf/ ¹⁷⁷ Hf of JMC 475 on MC-ICPMS	63
2.13	The separation of Rb, Sr and Nd using AG 50W- X8 and Ln-Spec resin	70
2.14	Measurement of ¹⁴³ Nd/ ¹⁴⁴ Nd of JMC 321 on MC-ICPMS	71
2.15	The accuracy of REEs concentrations measurements	75
2.16	Measurement of ⁸⁷ Sr/ ⁸⁶ Sr of NIST SRM 987 on MC-ICPMS	77
2.17	Measurement of ¹⁴³ Nd/ ¹⁴⁴ Nd of Merck on MC-ICPMS	78
3.1	The location map of the Godavari, Mahanadi and the Brahmani River systems	90
3.2	The monthly water and sediment discharge of the Godavari and the Mahanadi Rivers	93
3.3	The monsoonal rainfall patterns of the peninsular India river basins during 2013 and 2014	100
3.4	The TDS pattern in the Godavari, Mahanadi and the Brahmani Rivers	101
3.5	The intra annual variations of TDS in the Godavari River	103
3.6	Ternary plots of cations and anions in the Godavari, Mahanadi and the Brahmani River waters	105

37	The scatter plot of the total cation vs. CSI of the Godavari,	107
5.7	Mahanadi and the Brahmani River waters	107
3.8	The variability of dissolved ³⁷ Sr/ ³⁰ Sr in peninsular Indian	108
	Rivers from source towards sea The variations of the SEP variance from the Godeveri	
3.9	Mahanadi and the Brahmani River hasins	119
	The variations of the CER vs. runoff in the Godavari.	
3.10	Mahanadi and the Brahmani River basins.	120
2 1 1	The correlation of ⁸⁷ Sr/ ⁸⁶ Sr with the proxy of silicate	105
3.11	weathering, SiO ₂ /TDS in peninsular Indian River basins	125
3 1 2	The distribution of ⁸⁷ Sr/ ⁸⁶ Sr over Ca/Sr ratio present in	127
	peninsular Indian River waters	12,
3.13	Dissolved ^{or} Sr/ ⁵⁰ Sr in GRS vs. ^{or} Sr/ ⁵⁰ Sr of silicate phase of	128
	bed/bank and suspended sediments from the same location The distribution pattern of PAAS normalized PEEs of the	
3.14	Godavari and the Mahanadi River waters	131
	The funnel diagram of the GRS shows the spatial and inter-	
3.15	annual variations of the dissolved ε_{Nd}	132
210	Dissolved ε_{Nd} in GRS vs. ε_{Nd} of silicate phase of bed/bank and	100
3.10	suspended sediments from the same location	133
3 17	The scatter plot of Al normalized Mn with Fe of sediments	134
5.17	from the GRS	1.74
3.18	The ternary plot of the A-CN-K distribution pattern of	135
	sediments from the GRS	
3 10	of 87 Sr/ 86 Sr and s from the silicate phase samples of the	136
5.17	GRS	150
2 20	The distribution patterns of 87 Sr/ 86 Sr and ε_{Nd} with CIA and Al	100
3.20	wt% in from the GRS	138
2 21	The binary mixing plot of ε_{Nd} vs. 87 Sr/ 86 Sr in particulate phase	130
J.21	of the GRS	139
4.1	The concentration of REEs vs. salinity in the eastern Indian	155
	estuaries	
4.2	River normalized REEs vs. salinity in the eastern Indian	156
	The variations of SPM. Sr and Nd abundances and ⁸⁷ Sr/ ⁸⁶ Sr	
4.3	and ε_{Nd} in SPM along with the salinity gradient in the Ganga	158
	estuary	200
4.4	The distribution patterns of dissolved Mn in the East Indian	171
4.4	estuaries	101
4.5	The distribution patterns of dissolved Sr vs. salinity in the	162
	East Indian estuaries	_ • 4
4.6	I ne distribution patterns of Sr/Sr with 1/Sr in the East	163
47	Schematic diagram of submarine groundwater discharge into	165
 ./	Schematic diagram of submarine groundwater discharge lillo	103

(x **)**

coastal regions

	coustur regions	
4.8	The distribution patterns of ⁸⁷ Sr/ ⁸⁶ Sr with 1/Sr in the East Indian estuaries along with their end members	169
4.9	Ternary plot of contributions of seawater, riverwater and SGD near the Ganga, Krishna and the Godavari estuaries	172
4.10	The SGD water flux and the Sr flux through SGD in the East Indian estuaries	174
4.11	Al ₂ O ₃ -CaO+Na ₂ O-K ₂ O ternary diagram for the sediments in the East Indian estuaries	175
4.12	The Sr-Nd isotope mixing plot of SPM from the East Indian estuary.	176
4.13	The plot shows the river normalized Nd patterns in the East Indian Estuaries	178
4.14	The distribution of DO, dissolved Mn and Nd in the East Indian Estuaries	180
4.15	The distribution patterns in the concentration of the dissolved Nd and dissolved and particulate ε_{Nd} over salinity in the East	182
4.16	The PAAS normalized REEs of the East Indian Estuaries	184
5.1	The lithology map of the drainages of the Myanmar and Southern Thailand	190
5.2	Ternary plots FM-CN-K and A-CN-K of Andaman Shelf sediments	195
5.3	Scatter plot of 87 Sr/ 86 Sr and ϵ_{Nd} with Al ₂ O ₃ and CIA of the shelf sediments	197
5.4	Distribution patterns of 87 Sr/ 86 Sr and ε_{Nd} in the Western Myanmar, Northern and Eastern Andaman Basin	199
5.5	Binary mixing plot of Sr and Nd isotope composition of the sediments of the Andaman Shelf	202
5.6	The average rainfall pattern for the 5 years over the Andaman basin	204
5.7	Precipitation and elevation plotted along the three transects shown on DEM map following the SW monsoon track	206
6.1	The Hf and Nd isotope evolution over geological time scale	213
6.2	Cruise tracks and sampling locations in the Indian Ocean	215
6.3	Potential temperature and potential density plotted over salinity (θ -S- σ_q) in the Indian Ocean	217
6.4	Potential temperature and potential density plotted over salinity (θ -S- σ_q) in the Arabian Sea	219
6.5	The scatter plots of the basic parameters and concentration of Nd over the depth profiles in the Arabian Sea waters	227
6.6	The vertical profiles of dissolved Nd and Si in the Arabian Sea water column	228

6.7	The distribution pattern of dissolved Nd vs. Si present in the	229
	Arabian Sea water column	
6.8	The distribution pattern of concentration of (a) Nd and (b) Nd isotopic composition in the Arabian Sea water column.	230
6.9	The vertical profiles of Nd isotopic compositions in the Arabian Sea water column	232
6.10	The distribution patterns of various water masses present in the Arabian Sea	237
6.11	The distribution of excess Nd and its corresponding ε_{Nd} in the Arabian Sea waters column	243
6.12	The scatter plots of the basic parameters and concentration of Hf and sus over the depth profiles in the Arabian Sea waters	247
6.13	The vertical profiles of the basic parameters and concentration of Hf and $\varepsilon_{\rm Hf}$ over the depth in the Indian Ocean	248
6.14	The vertical distribution pattern of concentration of Hf and its isotope composition in the Arabian Sea water column	250
6.15	The distribution patterns of concentration of dissolved Hf and ε_{Hf} in the Indian Ocean	252
6.16	The vertical distribution of Hf isotopic compositions in the Indian Ocean along with the global ocean waters.	253

Chapter 1

Introduction

1.1. Introduction

Ocean productivity and ecosystem dynamics and hence the global carbon cycle and climate change are controlled by major nutrients present in the ocean. However, recent studies (Bruland et al., 1991; Coale, 1991; Morel et al., 1991; Biller and Bruland, 2012) have highlighted the important role of micro-nutrients (trace elements) in governing the productivity and the global carbon cycle, for example, deficiency of dissolved Fe in ocean limits the productivity in many regions of the global ocean. Thus, the availability of selected trace elements (such as Fe, Mn, Zn, Cd, and Cu) plays a key role in the ocean productivity (Saager et al., 1989; Middag et al., 2011; Biller and Bruland, 2012), carbon cycle and global climate change. Further, isotopes of many trace elements are used to study contemporary and paleo-oceanographic processes and paleo-productivity etc. For example, Nd isotopes of the seawater are being used routinely to track the various water masses present in a basin and also reconstruct the paleo-ocean circulation. In spite of their importance, the biogeochemistry of trace elements and isotopes (TEIs) in the global oceans is least understood and their distributions in the global oceans are poorly constrained. Their sources, sinks and internal cycling in the water columns are having a large uncertainty. Knowledge of the biogeochemistry of TEIs in the ocean is limited partly due to their lower concentrations making difficult to measure them as well as contamination during sampling of seawater. These problems have been circumvented by improved sampling and analytical techniques under the GEOTRACES program. The GEOTRACES program has been initiated globally to provide the detail distribution map of key TEIs in the modern global ocean after developing the sampling and measurement protocols of TEIs. In this thesis, an effort has been made to constrain the sources of selected trace elements and isotopes and their internal cycling in the Indian Ocean.

The dissolved chemical composition (i.e., nutrients, TEIs, etc.) of a given ocean basin is primarily regulated by five sources (Fig. 1.1). The fluvial river systems are the primary and principal supplier of dissolved, colloidal and particulate matter from weathering and erosion of the continental crust into the ocean. The second source is the processes acting in the estuary, coastal/shelf regions. The dissolution/desorption of the particulate matter and submarine groundwater discharge (SGD) in estuary/coastal regions contribute significant amount of trace elements to the ocean and is identified as a potential source of trace elements to oceans (Church, 1996; Moore, 2010; Rahaman et al., 2010; Rahaman and Singh, 2012; Beck et al., 2013; Garcia-Orellana et al., 2013; Rengarajan and Sarma, 2015; Jeandel, 2016). The abundances of dissolved and particulate matter are modified by removal and re-release of TEIs in the estuarine waters and coastal oceans. The relative significance of these sources depends on factors such as Eh and pH conditions prevailing in the estuaries. The aeolian dust originating from the adjacent landmasses (Fig. 1.1) is the third important source of trace elements to the ocean. Particles deposited on the ocean surface dissolve partially and contribute to trace metal budget of the ocean (Duce et al., 1991), and hence, the chemical and isotope composition of the surface waters reflect the dust signature depositing over them. Hydrothermal activity on the seafloor acts as a fourth source of TEIs to the global ocean (Fig. 1.1). Hydrothermal activity is the major source of some of the elements such as sulfur, zinc, copper etc. to the global ocean. Recently, it has been discovered that one of the very important source of dissolved Fe to the ocean is the hydrothermal activity (Mackey et al., 2002; Boyle et al., 2005; Tagliabue et al., 2010; Conway and John, 2014; Resing et al., 2015; German et al., 2016; Henderson, 2016; Homoky et al., 2016). The ocean circulation and the internal cycling are the fifth source of trace elements in a given basin, transporting water from one basin to another (Fig. 1.1). In addition, the global ocean circulation is an essential factor controlling and regulating the Earth's heat budget directing the Earth's climate change (Woods, 1985; Broecker, 1991).

The dissolved chemical composition in river waters is primarily controlled by the chemical weathering of minerals of rock/sediments present in the drainage basin, whereas, physical weathering controls the particulate composition.



Fig. 1.1: The cartoon shows various sources of TEIs in the ocean basin. Rivers, dust, estuary/shelf, hydrothermal and ocean circulations are important sources of TEIs to a given ocean basin. Five sources impacting the distribution of TEIs in a given basins are marked with 1 to 5 numbers and discussed in the text.

Several studies on the chemical weathering of various rivers over the world have shown that the silicate weathering of the continental crust regulates the climate change over million years time scale by consuming atmospheric CO₂ (Berner et al., 1983; Raymo and Ruddiman, 1992; Raymo, 1994; Ruddiman, 1997; Krishnaswami et al., 1999; Kump et al., 2000; Dessert et al., 2001; Amiotte-Suchet et al., 2003; Dessert et al., 2003; Huh, 2003; Das et al., 2005). It is well recognized that the ⁸⁷Sr/⁸⁶Sr ratio of the ocean has been gradually enhancing through the Cenozoic (Elderfield and Greaves, 1982; DePaolo and Ingram, 1985; Palmer and Elderfield, 1985; Elderfield, 1986; Goldstein and Jacobsen, 1988a; Hess et al., 1986; Veizer, 1989; Richter et al., 1992) which has been coupled with the increasing silicate weathering over the Himalaya supplying more radiogenic Sr (Edmond, 1992; Krishnaswami and Singh, 1998; Dessert et al., 2001; Dalai et al., 2003; Bickle et al., 2005; Das et al., 2005; Rengarajan et al., 2009). In particular, several studies have been carried out on the erosion/weathering processes operating over the Himalaya and elemental and isotope fluxes delivered by the Himalayan rivers to the northern Indian Oceans (Sarin and Krishnaswami, 1984; Sarin et al., 1989, 1992; Krishnaswami et al., 1992, 1999; Palmer and Edmond, 1992; Edmond and Huh, 1997; Galy and France-Lanord, 1999; Dessert et al., 2001; Dalai et al., 2002; Singh and France-Lanord, 2002; Bickle et al., 2003, 2005; Das et al., 2005; Singh et al., 2005, 2006; Rai and Singh, 2007; Rengarajan et al., 2009; Tripathy et al., 2011). Considering that, there are only a few studies in the peninsular Indian drainage having very diverse lithology and climate, an effort is made to assess the impact of chemical weathering on chemical and Sr-Nd isotope compositions of dissolved and particulates from the Peninsular Indian Rivers by studying a couple of major peninsular rivers viz. the Godavari, Mahanadi and the Brahmani and their tributaries. Both physical and chemical weathering processes and factors influencing them in these basins are studied using major and trace elemental chemical composition along with Sr and Nd isotope composition. Fluxes of various elements and isotopes emanating from these basins have been quantified using the chemical composition and water/sediment discharges of the rivers draining these basins. Impacts of these fluxes on their global oceanic budget are assessed.

In addition to the riverine sources of nutrients and TEIs to the ocean, estuaries and SGD near the estuaries and coast also act as potential sources (Church et al., 1996; Krest et al., 2000; Windom et al., 2000, 2006; Moore, 2010; Rahaman et al., 2010; Rahaman and Singh, 2012; Beck et al., 2013; Garcia-Orellana et al., 2013; Rengarajan and Sarma, 2015). Estuaries modify the dissolved and particle composition brought by riverine flow and SGD by removal and re-release of TEIs to the estuarine waters and ultimately to the open oceans. The relative significance of these sources is exceptional for each trace metal and depends on factors such as their solubility during weathering and erosion and their chemical behavior in rivers, estuaries, and oceans. The uncertainties which exist in the input sources like rivers, aeolian dust and estuaries to the ocean can be understood by evaluating their TEIs behavior. These studies also help to understand the marine biogeochemistry.

Recent studies recognized that, SGD also is a privileged pathway together with the riverine, aeolian and anthropogenic suppliers of chemical compositions to the marine environments (Basu et al., 2001; Burnett et al. 2002; Charette and Sholkovitz, 2006; Paytan et al., 2006; Lin et al., 2010; Moore, 2010; Huang et al., 2011; Johannesson et al., 2011; Rahaman and Singh, 2012; Beck et al., 2013; Kotwicki et al., 2014; Garcia-Orellana et al., 2014; Rengarajan and Sarma, 2015). The SGD defined as groundwater seepage through continental shelf sediments includes both terrestrial and marine groundwater from the sea with emphasis on the coastal zone (Burnett et al., 2003), where the biogeochemical reactions modify the water chemistry (Moore, 2010). The groundwater seepage towards the coastal zone has been suggested as a potential source of nutrients (Krest et al., 2000), trace metals (Windom et al., 2006), natural radio nuclides (Garcia-Orellana et al., 2013) including Sr (Basu et al., 2001; Charette and Sholkovitz, 2006; Paytan et al., 2006; Lin et al., 2010; Moore, 2010; Huang et al., 2011; Johannesson et al., 2011; Rahaman and Singh, 2012; Beck et al., 2013). SGD leads the biogeochemical processes to the estuary and ultimately to the open ocean. The estimation of groundwater seepage to the coastal waters can be obtained with the use of naturally occurring geochemical tracers which are considered as fingerprint proxies. An advantage of groundwater tracers is that they show an integrated signal while entering into the marine water column via various pathways in the aquifer. Several studies on SGD in the past used the natural radium isotopes (²²³Ra, ²²⁴Ra, ²²⁸Ra and ²²⁶Ra) and ²²²Rn to assess the groundwater discharge into the ocean (Burnett et al. 2002; Kim and Hwang, 2002; Burnett et al., 2003, 2006; Garcia-Orellana et al., 2014; Rengarajan and Sarma, 2015). In a study state, the addition of radium fluxes is balanced by the decay of radioactive radium isotopes and mixes in the estuaries. The present study investigated the distributions of dissolved Sr concentrations and its isotope ratios in four eastern Indian estuaries to understand their behavior and flux to the Bay of Bengal (BoB) which is directly relevant to the Sr budget and the evolution of ⁸⁷Sr/⁸⁶Sr in the oceans. The previous studies inferred that the Sr isotope composition of paleo-seawater archived in marine deposits is being used for stratigraphic correlation, chronology and also to infer about the impact of temporal variability in both tectonics and climate on the isotope evolution. So, it is important to have knowledge about the budget of oceanic Sr and ⁸⁷Sr/⁸⁶Sr along with their sources and sinks in the oceans (Colin et al., 1999; Davis et al., 2003; Allegre et al., 2010; Tripathy et al., 2011).

One of the major uncertainties in the determination of the elemental and isotope fluxes from the continents to the ocean is the impact of the transition zone, the estuaries, on them. Behavior of various elements in the estuaries is quite variable. Some of the elements such as Re, U, B, Sr etc. are highly conservative (Rahaman et al., 2010; Rahaman and Singh, 2010, 2012) and pass these gauntlet without any modification and vary linearly with salinity, whereas many of the elements get modified significantly in these estuaries as some of them get sequestered (such as REEs) (Boyle et al., 1974; Eckert and Sholkovitz, 1976; Kim and Kim, 2015; Rousseau et al., 2015) while others are released (such as Ba, Nd, Mn) depending on Eh, pH condition prevailing in them (Hatje et al., 2003; O'Connor et al., 2015). Concentration of Rare Earth Elements (REEs) and

Neodymium (Nd) isotopic composition (ε_{Nd}) are of immense importance to trace the modern Ocean water masses, their present and paleo-oceanographic circulations, biogeochemical processes and their potential sources like riverine, aeolian, sediments dissolution and hydrothermal activities (Martin et al., 1976; Elderfield and Greaves, 1982; Jeandel, 1993; Sholkovitz and Szymczak, 2000; Rousseau et al., 2015; German et al., 2016; Henderson, 2016; Homoky et al., 2016). Several studies were carried out to study the behavior of dissolved REE concentrations in estuaries and recognized that the REEs get removed significantly from the dissolved phase in the low salinity zones and get released back mildly in mid to high salinity zones (Martin et al., 1976; Hoyle et al., 1984; Goldstein and Jacobsen, 1988b, c; Elderfield et al., 1990; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000; Rousseau et al., 2015). The trace element (e.g. Fe, Mn, and REEs) removal in mixing zones might be because of coagulation of river colloids in low salinity zones, adsorption of trace elements onto the suspended particulates and/or Fe-Mn oxyhydroxides, destabilization of mixed iron oxide-organic matter colloids during mixing with seawater. The release and re-supply of trace elements in the estuaries is attributed to the dissolution and/or desorption of suspended particulate matter (SPM), Fe-Mn oxyhydroxides and contribution from SGD (Coonley et al., 1971; Sholkovitz, 1976; Yeats and Bewers, 1976; Boyle et al., 1977; Sholkovitz and Szymczak, 2000; Kim and Kim, 2014; Rousseau et al., 2015). This release of dissolved REEs is important for their global budgets and hence their estimation in all the estuaries is required. Behavior of REEs and Nd isotopes in some of the global estuaries including the Amazon have been studied (Goldstein and Jacobsen, 1988b; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000; Åstrom, 2012; Rousseau et al., 2015), however, very little have been done to know their behavior in tropical and monsoon-dominated estuaries with huge sediment discharge where their behavior could be entirely different compared to sub-tropical and polar estuaries (Rahaman et al., 2010; Rahaman and Singh, 2012). Behavior of REEs and Nd isotope composition in some of the Indian estuaries related to the BoB such as the Ganga (Hooghly), Mahanadi, Krishna and the Godavari has been studied in this thesis to estimate their net loss/gain and final fluxes to the BoB and to assess the impact on their global budgets. In addition, the processes operating in these estuaries controlling the abundances of TEIs have been evaluated.

The chemical composition of seawater is also regulated by the processes operating on the sediments of the shelf region and knowledge of sources of sediment, their chemical and isotope composition and factors influence their provenance, dispersion and deposition are required. It is well recognized that rivers are the primary transporters of physically and/or chemically weathered continental materials to the shelf region. They play a prominent role in the evolution of coastal sediments. Terrigenous sediments eroded from the Himalaya, Myanmar, and Indo-Burman subcontinents are deposited to the Andaman Sea by rivers such as the Irrawaddy (Ayeyarwaddy), Salween (Thanlwin), Sittang, Kaladan and the Tanintharyi etc. The Irrawaddy is the third largest river in the world in terms of suspended sediment discharge. Together with the Salween, it contributes ~550 million tons (MT) of sediment annually to the ocean (Robinson et al., 2007). Intense monsoon causes higher runoff in the Irrawaddy Basin, which in turn enhances erosion in the catchment area. The sediments brought by the Irrawaddy and the Salween Rivers are deposited in the Northern and Eastern shelf of the Andaman Sea with a width of more than 170 km. A significant amount of terrestrial organic matter brought by these rivers is deposited along with them influencing the long-term carbon cycle (France-Lanord and Derry, 1997; Bird et al., 2008; Ramaswamy et al., 2008). The sources of these sediments deposited on the Northern and Eastern shelf of the Andaman Sea and the factors controlling the erosion of this large volume of sediments are poorly constrained due to complicated logistic and political reasons associated with the sampling. The seasonally reversing surface circulation controlled by the monsoon (Rodolfo, 1969; Ramaswamy et al., 2004; Rao et al., 2005) influences the dispersion and deposition of these sediments significantly. Influence of the Irrawaddy and the Salween Rivers on the sedimentary budget of the eastern BoB is still a matter of debate, though they deliver a huge amount of sediments into the Andaman Sea (Rao et al., 2005; Robinson et al., 2007). The deposited sediments in the Andaman Sea brought down by these river systems, preserve imprints of the erosion and weathering history of the Himalayan and the Burman Ranges (Colin et al., 1999). Detrital sediments are primarily the weathered products of continental rocks with a wide range of Sr and Nd isotope ratios. The distinct isotopic compositions of these sediments can be used to track their provenance (Goldstein et al., 1984; Colin et al., 1999; Galy and France-Lanord, 2001; Singh and France-Lanord, 2002; Singh et al., 2008; Tripathy et al., 2011; Goswami et al., 2012). In the present study, the Sr and Nd isotopic composition and major elemental concentrations of silicate fractions of surface sediments of the Northern and Eastern shelf of Andaman Sea are measured to track their provenances. Further, an effort is made to evaluate the role of climate and tectonics in controlling the erosion in its catchment and to assess the impact of surface ocean circulation in controlling the dispersal and deposition of these sediments.

Global ocean circulation plays a vital role in controlling and regulating Earth's heat and ocean nutrient budget. Furthermore, ocean circulation helps in regulating various other chemical properties such as dissolved oxygen (DO), trace elements and isotopes etc. by transporting them from one ocean basin to another. As a consequence, by studying the water masses in the ocean, the rate and transport properties in the ocean can be understood. The global ocean circulation known as conveyor belt/thermohaline circulation originates around the Northern Atlantic continent by sinking of cold and saline water masses at high latitudes known as North Atlantic Deep Water (NADW; Fig. 1.2; Gordon, 1986; Broecker, 1991; Rhein, 1995). The NADW forms at a depth of about 2000 to 3000 m with a specific characterized salinity and temperature and flows towards the south (Frank, 2002). In the vicinity of the Antarctic continent, Antarctic Bottom Water (AABW) with higher density and Antarctic Intermediate Water (AAIW) with lower density forms and flows towards North. Due to the density differences, the AABW exists below the NADW; AAIW is sandwiched between NADW and its surface waters.



Fig. 1.2: The generalized modern global ocean circulations. The blue line indicates the high saline and highdensity waters (cold path) originated in the North Atlantic as NADW and AABW which forms near the Southern Ocean. The NADW and AABW together form ACC around the Antarctic which distributes the deep and bottom waters throughout the world ocean. The red line indicates the shallow current (warm path) of the global ocean. As a consequence of upwelling, the global ocean surface waters originate and become warm in the Indian and North Pacific Ocean. However, the warm surface waters return to the Atlantic Ocean due to

Indonesian Through Flow (ITF) and atmospheric wind patterns. The white colored lines on continents represent a few global major rivers. This figure modified after Broecker, (1991) and Rahmstorf, (2002).

The NADW, AAIW, and AABWs are eventually advected into the Antarctic Circumpolar Current (ACC) and form Circumpolar Deep Water (CDW) which flows into the Indian and Pacific Oceans as NADW and AABW (Frank, 2002). In the Northern Indian and Pacific Oceans, upwelling brings the deep and bottom waters to the surface and subsurface. The Pacific-Indonesian Through Flow (ITF) regulates the warm surface and subsurface waters of the Indian Ocean. Water masses present in the Atlantic and Pacific Oceans are well studied (Jeandel, 1993; Goldstein and Hemming, 2003; Amakawa et al., 2004) to a large extent, however, their knowledge in the Indian Ocean is very limited (Jeandel et al., 1998; Amakawa et al., 2000; Singh et al., 2012; Goswami et al., 2014). The pathways of the deep and bottom waters and their upwelling in the Indian Ocean are a matter of debate (Wyrtki, 1973; Piotrowski et al., 2009). Some of the earlier studies pertaining to water mass identification and their movement in the Indian Ocean (Jeandel et al., 1998; Amakawa et al., 2000; Piotrowski et al., 2009) are based on chemical tracers, which have been proved to be non-conservative. Nd and Hf isotope compositions of the seawater are found to be faithful tracers of the different water masses owing to their characteristics signatures for different water masses. The Neodymium and Hafnium (Hf) isotope compositions show huge variations in their inputs to the global ocean and have been usually served to identify the changes in oceanographic circulation patterns and weathering contributions resulting from tectonic and climatic factors (Frank, 2002; Goldstein and Hemming, 2003). The decay of ¹⁷⁶Lu with a half-life ($t_{1/2}$) of 37.1 × 10¹⁰ yr produces ¹⁷⁶Hf, and thus there are large variations in ¹⁷⁶Hf/¹⁷⁷Hf within crustal rocks as a function of age and Lu/Hf fractionation. Similarly, the decay of ¹⁴⁷Sm with a half-life of 106×10^{10} yr leads to the production of ¹⁴³Nd, resulting in the variations in ¹⁴³Nd/¹⁴⁴Nd.

The Nd and Hf isotope systems are expressed in the ϵ -notation, which in the case of Nd is calculated as:

In the case of Hf, it is calculated as:

where, the subscript CHUR represents the Chondritic Uniform Reservoir $[0.512638 \text{ for } {}^{143}\text{Nd}/{}^{144}\text{Nd}$ (Jacobsen and Wasserburg, 1980) and 0.282769 for ${}^{176}\text{Hf}/{}^{177}\text{Hf}$ (Nowell et al., 1998)] for the present day.

Radiogenic Hf and Nd isotopes are extensively being used as water mass proxies to study ocean circulations and to examine their sources. Nutrients, Fe, Mn, Cd, Ba, Zn and radiogenic isotopes of Nd and Hf provide very good proxies to study ocean circulation as their distributions are governed by mixing processes in the ocean. Unlike nutrients, Cd, Ba, and Zn, isotopic compositions of Nd and Hf cannot be modified chemically and biologically and are conservative in the water column. Moreover, the residence time of Nd and Hf in the ocean is of the order of or less than ocean mixing time (~500-1500 years) making them a suitable proxy of ocean water circulation. The variations of Hf isotopic compositions (ϵ_{Hf}) are twice that of Nd isotopic compositions (ϵ_{Nd}) due to mantle melting and its marginally higher residence time (1000-1500 years) than that of Neodymium (500-1000 years). The pattern and rate of ocean circulation generate spatial variation in the distribution of Nd and Hf isotopes which can be used to reconstruct the ocean circulation that brings about these variations. Therefore, the Nd and Hf isotopic compositions of the water masses are one of the best proxies
to study the ocean circulation due to their suitable residence time and nature to acquire and preserve the source signature (Frank, 2002; Goldstein and Hemming, 2003). There have been a few studies on the REEs concentrations, Nd isotopic composition of seawater, primarily focused in the Arctic, Atlantic, Pacific and the Indian Oceans (Jacobsen and Wasserburg, 1980; German and Elderfield, 1990; Bertram and Elderfield, 1993; Jeandel, 1993; Jeandel et al., 1998; Amakawa et al., 2000, 2004; Nozaki and Alibo, 2003; Singh et al., 2012; Goswami et al., 2014; Haley et al., 2014; Hathorne et al., 2015). Very little is known about the water mass structure and various water masses formed in the Indian Ocean, particularly that of deeper waters in the northern Indian Ocean (Amakawa et al., 2000; Nozaki and Alibo, 2003; Singh et al., 2012; Goswami et al., 2014). The limited studies on Nd isotopic composition of seawater from the Indian Ocean suggest that it is intermediate to that of the Atlantic and the Pacific Oceans. The Hf isotopic study is far more limited than the study of Nd isotopes in the ocean, mainly due to measurement difficulties (Godfrey et al., 2009; Rickli et al., 2009; Zimmermann et al., 2009a, b; Stichel et al., 2012). It has been suggested that during continental weathering, Hf isotopic composition can exhibit large variability due to selective retention of unradiogenic Hf in the resistant mineral zircon (in which Lu/Hf ratio will be low), which tends to be concentrated in coarse coastal and fluvial sands (Lee et al., 1999; Frank, 2002; Goldstein and Hemming, 2003). The Hf in the zircons of the sand fraction is almost unavailable to weathering and is not introduced into seawater. Therefore, the seawater data as represented by ferromanganese crust/nodule data has higher ε_{Hf} for a given ε_{Nd} (Godfrey et al., 1997; Albare`de et al., 1998; Lee et al., 1999; Piotrowski et al., 2000; David et al., 2001; van de Flierdt et al., 2004a, b, 2006). In this study isotope compositions of Nd and Hf are being used to study the ocean circulation, identify the water masses present in the Arabian Sea and the Indian Ocean and quantify the additional sources of Nd to the Arabian Sea using inverse modeling.

In short the focus of my thesis work is to study (i) the chemical weathering processes in the peninsular rivers, the Godavari, Mahanadi and the Brahmani River systems to understand weathering and erosion processes occurring in the basin and to estimate the fluxes of TEIs from these basin to the nearby ocean, (ii) the behavior of selected TEIs in the east Indian Estuaries, to understand their source/sink nature such as processes of adsorption/desorption, SGD supplying the TEIs to the ocean, (iii) the sources of sediments to the northern Andaman Shelf, their dispersal and deposition pattern and factors influencing them, and (iv) to characterize water masses present in the Arabian Sea and the eastern Indian Ocean using radiogenic tracers, such as ε_{Hf} and ε_{Nd} . Together these will be useful to assess the impact of regional geology, hydrology, climate and sedimentology on the oceanic budget of REEs, isotopes of Hf and Nd.

1.2. Objectives

The basic objectives of my thesis are:

i. Understand the weathering/erosion processes occurring in the Peninsular Indian drainage, factors influencing them and the fluxes of selected trace elements and isotopes supplied from these basins to the Bay of Bengal and their impact on global budgets.

ii. Study the behavior of REEs, Mn, Sr and Sr-Nd isotope composition in the tropical, monsoon-fed estuaries of India related to the Bay of Bengal and to estimate their net fluxes to the open ocean.

iii. Track the provenance of sediments deposited in the Andaman Shelf and to evaluate the role of climate, ocean circulation etc. in influencing the depositional pattern.

iv. To study the geochemical budget of Nd and Hf in the Arabian Sea and to assess the structure of water masses present in it and sources of Nd controlling its budget in the Indian Ocean.

1.3. Study Area

To fulfill the above objectives, study area includes the peninsular Indian River basins, estuaries situated in the east coast of India, shelf region of the Northern Andaman and the Arabian Sea and the eastern Indian Ocean. Sediment and water samples were collected from these areas to emphasize the role of rivers, estuaries, shelf region and the ocean circulation in controlling the biogeochemistry of trace elements and isotopes of the Indian Ocean.

1.4. Structure of the thesis

The present thesis consists of seven chapters.

Chapter 1: Introduction

This chapter provides the current understanding about the erosion and weathering in the peninsular basin and the related outstanding problems. The behavior of various trace elements in the estuaries and processes impacting their distributions are discussed and need for studying the REEs, Mn, Sr and Nd and Sr isotope compositions in the Indian estuaries are emphasized. In addition, the impact of water and sediment fluxes from the Irrawaddy River on the shelf sediments are described in this chapter with special reference to tectonics, climate and surface ocean currents. This chapter gives an overview of global ocean circulation, the sources of dissolved and particulate chemical composition to the global ocean and the primary information of those sources. Detailed discussions on paleooceanographic tracers, like, Hf-Nd isotopic compositions are also introduced. The objectives of the thesis are also described in this chapter.

Chapter 2: Materials and Methods

Chapter 2 presents the detailed materials and analytical methodology used in this thesis. This chapter is divided into three sections which are (i) the study area, (ii) the geological settings present in this study and (iii) the chemical procedures and the analysis of the major, trace elements concentrations and Sr-Nd-Hf isotope systems present in the natural waters and sediments. This chapter provides basically a "cookbook" for the consistent and reliable extraction and measurement protocols of major and trace elements concentrations and Sr, Nd and Hf isotope compositions from the natural water and sediment samples. As the Hf isotope measurement was carried out for the first time as a part of this thesis, a detailed

discussion about its chemical separation and mass spectrometric measurements are provided in this chapter.

Chapter 3: Erosion and Weathering in the Peninsular Indian Rivers and Fluxes to the Bay of Bengal

Chapter 3 provides the results and discussions of the study of dissolved and particulate elemental and isotope geochemistry of the Godavari, Mahanadi, and the Brahmani Rivers, which flows through peninsular India into the BoB. This chapter explains the chemical weathering rate and CO_2 consumption rates and discusses the relative impact of different factors such as lithology and runoff on the dissolved chemical composition in the Godavari, Mahanadi and the Brahmani Rivers using inverse and forward modeling, respectively.

Chapter 4: Behavior Trace Elements and Isotopes in the East India Estuaries: Implications to Their Global Marine Budget

In chapter 4, the TEIs behavior in waters and particulate matters from Eastern India Estuaries namely the Ganga (Hooghly), Mahanadi, Krishna and the Godavari have been provided. This chapter also confers the information of the chemical flux through the submarine groundwater discharge (SGD) and particles absorption, desorption and/or dissolution behavior and their implications for global marine budget.

Chapter 5: Lithology, Monsoon and Sea-Surface Current Control on Provenance, Dispersal and Deposition of Sediments over the Andaman Continental Shelf

Chapter 5 contains the comprehensive information of the sediments deposition and dispersal in the Andaman Basin. This chapter also provides the sequence of sediment sources and factors controlling the composition of sediments present in the Andaman basin like lithology, rainfall, runoff and relief.

Chapter 6: Dissolved Hf and Nd concentration and their isotopic compositions in the Indian Ocean: Implications to water-particles interaction, upwelling's, water mass mixing and their sources

Chapter 6 provides the detailed information over the water masses and its distribution patterns present in the Arabian Sea and the Eastern Indian Ocean using multiple physical (T-S diagrams) and chemical proxies such as Hf and Nd concentrations and Hf-Nd isotope compositions based on their differences in their water column. Further, this chapter also provides information pertaining to the various sources contributing water masses to the Arabian Sea and their contributions to TEIs flux using inverse modeling results calculated using dissolved Nd concentrations and its isotopic compositions.

Chapter 7: Conclusions and future Perspectives

Finally, chapter 7 concludes the major outcomes of the present thesis and also provides the future research scope emanating from studies.

Chapter 2

Materials and Methods

The present thesis aims at understanding continental weathering and transport of trace elements and isotopes (TEIs) through fluvial river systems, behavior of TEIs in the East Indian Estuaries and impact of ocean circulations and the biogeochemical processes on them in Open Ocean and to track the various water masses present in the Indian Ocean using these TEIs. The objectives of this study, as described in Chapter 1, are to determine (i) the spatial and temporal variability of physical and chemical erosion in the Godavari, Mahanadi and the Brahmani River systems (Fig. 2.1) using major and trace elements and radiogenic isotopic (⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd) composition of their dissolved and particulate phases (ii) the behavior of TEIs in the mixing zones of the Ganga (Hooghly), Mahanadi, Krishna and the Godavari (Fig. 2.1) and implications to their global ocean budgets (iii) the factors influencing the supply of sediments and their sources to Andaman Sea shelf region (Fig. 2.1) and finally (iv) to identify the various water masses in the Arabian Sea and in the Indian Ocean (Fig. 2.1) using dissolved Hf-Nd isotopic compositions (ε_{Hf} and ε_{Nd}) and to understand the biogeochemical processes controlling their distributions in the ocean in addition to water masses and ocean circulation. Sampling strategies and measurement protocols in this study are adopted keeping the above objectives in mind, which are detailed in the following sections.

2.1 Study Area

The various peninsular Indian River systems, the East Indian estuaries, and Indian Ocean sampling tracks carried out in this study are shown in Fig. 2.1. The major tropical rivers like the Godavari, Krishna, Mahanadi, Brahmani and the Cauvery are east flowing while Narmada, Tapi, Mahi and the Mandovi are west flowing rivers and drain 43% of the total geographical area of India $(3.23 \times 10^6 \text{ km}^2, \text{Panda et al., 2011})$. Tropical rivers like the Godavari, Narmada, Mahanadi, Brahmani, Tapi and the Mahi draining the central Indian region (with an average annual flow of 1869 km³) erode significantly higher sediment load than the Krishna, Cauvery, and the Pennar (east flowing) Rivers that drain south Indian

region. These tropical rivers undergo severe physical and chemical weathering and control the long-term atmospheric CO_2 as well as the Earth's heat budget (Rao, 1975; Jain et al., 2007; Panda et al., 2011).



Fig.2.1: Overview map of the study area wherein the purple, dark blue and dark red lines are cruise tracks SS-300 in the Arabian Sea, SK 304 in the Indian Ocean and SM-24-13 in the Hooghly coastal regions respectively. Major rivers flowing through the Indian continent (the Ganga-Brahmaputra (G-B), Godavari, Krishna, Indus and the Narmada Rivers etc.) and the Burman regions (the Irrawaddy and the Salween Rivers) debouching into Northern Indian Ocean are marked as white lines.

2.1.1 Godavari River System

After G-B River system, the Godavari is the third largest river in India in terms of water and sediment discharge. The Godavari River rises in the Sahyadris

near Triambakeswar, about 80 km east of the Arabian Sea eastern shoreline, at an elevation of 1,067 m (Rao, 1975; Jha et al., 2009; Panda et al., 2011) and discharges into the Bay of Bengal (BoB) at North of Rajahmundry, Andhra Pradesh after flowing (in general east and southeast directions) a distance of 1,465 km (Table 2.1). The Godavari River basin lies between latitudes 16°16' N to 22°36' N and longitudes 73°26' E to 83°07' E. The basin has a catchment area of 312,813 km², which covers around 10% of the total geographical area of India (Biksham, and Subramanian, 1980; Jha et al., 2009).



Fig. 2.2: Sample location map of the Godavari River System. The sampling has been conducted in two consecutive (2013 and 2014) monsoon periods.

The Pravara, Purna, Manjira, Maner, Peddavagu, Kaddam, Pranhita, Indrāvati and the Sabari are the major tributaries of the Godavari River System (GRS). The Godavari River debouches its dissolved and particulate matter into the Bay of Bengal (BoB) by splitting into two distributaries namely the Gautami (near Yanam) and the Vasishta (near Antarvedi). During summers the temperature of the GRS varies between 30 and 34 °C with a maximum of 47 °C in April-May whereas, in winters from 16 to 24 °C with a minimum of 10 °C in December. The average annual rainfall to the GRS is ~100 cm and it occurs mostly (~85%) during monsoons (June to October) (<u>http://giovanni.gsfc.nasa.gov/giovanni/</u>). The annual average water discharge of the Godavari River is about 1.1×10^{14} L (Rao, 1975; Gupta et al., 1997; Jha et al., 2009; <u>http://www.compositerunoff.sr.unh.edu/</u>) of which 85% occurs during the monsoon season (Sarin et al., 2002). The annual average sediment discharge is around 170 million tons (MT) of which 95% drains in the monsoon season (Biksham and Subramanian, 1988a, b; Panda et al., 2011).

2.1.2 Mahanadi and Brahmani River Systems

The Mahanadi and the Brahmani Rivers are two major adjacent rivers in Odisha and drain through similar lithology. The Mahanadi River (Table 2.6; Fig. 2.3) originates near Pharsiya village in Raipur district, Chhattisgarh at an elevation of 442 m (Table 2.1). It is the second most important peninsular river post GRS with respect to water and sediment flux and flows from west to east draining into the BoB. The Mahanadi River extends between latitude 19°20' N and 23°35' N and longitudes 80°30' E and 86°50' E with a drainage area of 141,589 km² (Table 2.1) occupying 4.3% of total Indian geographical area (Rao, 1975; Chakrapani and Subramanian., 1990; Jain et al., 2007). The total length of the Mahanadi River from its origin to its outflow into the BoB is 857 km of which 357 km flows through Chhattisgarh and remaining 500 km flows in Odisha. The Seonath, Hasdo, Jonk, Mand, Ib, Ong and the Tel are the leading tributaries of the Mahanadi River basin. The average temperature of the head-waters of the Mahanadi River basin varies between 12 to 40 °C, whereas, the downstream temperatures vary from 14 to 40 $^{\circ}$ C and the temperature variation near the sea is from 16 to 32 °C. The annual average rainfall of the Mahanadi River catchment is 142 cm and it happens mostly during the monsoon (90%).

Name of River	Elevation	levation Length Area I		Rainfall	Discharge	SPM
	m	km	10^3 sq. km	cm yr ⁻¹	$10^{12} \text{ L yr}^{-1}$	MT yr ⁻¹
		Godava	ari River Syst	em		
Pravara	1050	208	6.54	60.9	1.98	
Purna	838	374	15.58	79.7	2.83	
Manjira	823	686	30.84	84.6	0.01	
Peddavagu	547	70	1.67	120.0	0.90	
Kaddam	380	86	2.63	80.0	0.22	
Pranhita	640	721	109.08	136.3	36.81	
Indravati	914	536	41.66	158.8	32.85	
Sabari	1372	418	20.43	143.2	14	
Godavari Basin	1062	1465	315.43	113.2	105	170
	Mahana	adi (MND) River Syste	m		
Seonath	533	290	30.76	130	14.64	
Hasdeo	915	333	9.86	115	4.34	
Jonk	700	182	3.48	140	1.70	
Mand	686	220	5.20	105	2.13	
Ib	762	251	12.45	125	3.72	
Upper MND			21.65		45.88	
Ong	457	204	5.13	165	3.26	
Tel		296	22.82	155	13.51	
Middle MND			12.65		13.47	
Lower MND			17.59		11.76	
Mahanadi	442	857	141.59	150	70.48	60
	Bra	hmani Ri	ver System			
Koel	762	260	9.10	110	2.78	
Sankha	1000	240	6.97	120	5.25	
Brahmani	600	799	39.03	130	18.31	5.22
Krishna River	1337	1400	258.95	78.4	30	64
Ganga River	3892	2525	862.77	120	380	500
All data from t	the compile	tion of	Biksham and	d Subrama	anian 1988a	and b:

Table 2.1: The Physical details of the peninsular river systems

All data from the compilation of Biksham and Subramanian, 1988a, and b; Trivedi et al., 1995; Gupta et al., 1997; Galy et al., 1999; Singh and France-Lanord, 2002; Singh et al., 2008, http://www.cwc.nic.in/, and Arc GIS.

The average annual water flow of the Mahanadi River is 6.7×10^{13} L (Table 2.1) of which more than 90% occurs during the months of June-October (monsoon). The mean annual sediment discharge of the Mahanadi River is 30.7 MT (Table





Fig. 2.3: The detailed sampling locations of the Mahanadi and the Brahmani Rivers and their tributaries. Sampling has been done during monsoon, 2014.

The Brahmani River (Fig. 2.3) is the largest river in the state of Odisha after the Mahanadi River. The Brahmani River takes its name near Vedvyas, Panposh in the Odisha after the confluence of the Sankh (originates in Chhattisgarh at an elevation of 1000 m) and the Koel Rivers (rises in Jharkhand at an elevation of 762 m). After confluence, the Brahmani River moves towards southeast (SE) direction and discharges into the BoB. The Brahmani River geographically exists between 20°28' to 23°38' N and 83°55' to 87°3' E (http://india-wris.nrsc.gov.in/). It travels a length of 799 km and drains an area of 39,269 km² with annual average water and sediment discharges of 2.85×10^{13} L and 20.4 MT (Table 2.1) respectively. The Brahmani River basin annually receives about 135 cm of rainfall; the average annual humidity is 66% and the



temperature variation is between 11.9 and 44.4 °C (Rao, 1975; Jain et al., 2007; Sundaray, 2010; Panda et al., 2011; Parwin, 2014).

Fig. 2.4: The detailed sampling locations of the Ganga, Mahanadi, Krishna and Godavari Estuaries (Monsoon, 2013).

2.1.3 East Indian Estuaries

Estuaries play an essential role in transporting nutrients and TEIs of both the dissolved and particulate phases of the rivers and ground water to the marine shelf region and ultimately to the open ocean. The Estuaries, also act as reactors of marine biogeochemical processes. The mixing zones of East Coast of India i.e., the Ganga (Hooghly), Mahanadi, Krishna and the Godavari Rivers studied in this thesis are listed in Table 2.7 and shown in Fig. 2.4.

The Ganga originates in the Himalaya and drains through a mixture of lithologies viz. granite/gneisses, shales, black shales, slates and carbonates and alluvium in the Ganga plain. The Hooghly is one of the distributaries of the Ganga, bifurcates near Farakka and flows into the BoB (Fig. 2.4a). The water discharge in the Hooghly River is regulated from the Farakka barrage to maintain water levels with average annual water discharge of 5.0×10^{13} L (Rahaman et al., 2010; Sarma et al., 2012).

The Godavari and the Mahanadi Rivers systems have been discussed in the sections 2.1.1 and 2.1.2, respectively.

The Krishna River rises in the Western Ghats of India, near Mahabaleswar and drains through peninsular Indian shield into the BoB. Deccan traps, Precambrian and Dharwar formations and recent alluvium occupy its drainage basin. The entire drainage basin covers an area of 2.6 x 10^5 km² and the mean annual water discharge of Krishna at Vijayawada (Fig. 2.4b) is 6.0 x 10^{13} L (UNESCO 1971; <u>http://www.grdc.sr.unh.edu/</u>).

2.1.4 Andaman Shelf Basin

Andaman is a unique marine basin, which is deviated from the BoB by Andaman-Nicobar Ridge. The Irrawaddy and the Salween Rivers are the major sedimentary sources to the Andaman Basin. Together they supply ~550 MT sediment load to the Andaman Sea annually. The Irrawaddy River mouths cover



Fig. 2.5: Sampling locations (numbers) map of the northern Andaman Sea and Gulf of Martaban overlain on DEM hillshades colour scale elevation/depth (m) map.

about 170 km of shelf width and increases to more than 250 km in the center of the Gulf of Martaban (Fig. 2.5). A N-S trending 120 km wide bathymetric depression is present towards the southern end of the continental shelf and the Martaban submarine canyon lies within this depression (Rao et al., 2005).

The tidal and the seasonally reversing monsoon currents strongly influence the sediment spreading on the Irrawaddy continental shelf (Wyrtki, 1973; Ramaswamy et al., 2004; Rao et al., 2005). The southwest (SW) monsoon is active during May-October and 80 to 90% of the annual Burmese rainfall, runoff, and sediment discharge occurs in this period, whereas the north-east (NE) monsoon is active between December and February (Rodolfo, 1969; Rao et al., 2005). During SW monsoon, Myanmar receives very high precipitation and at places it is highly intense and focused. The western slopes of the Indo-Burmese and western/central granitic ranges receive rainfall as high as 5 m y⁻¹ (Damodararao et al., 2016). The higher precipitation in the catchment produces the higher erosion and transport a large quantity of sediments to the Andaman Sea. The majority of the sediments are delivered to the sea during SW monsoon period (Win, 2011) from the Irrawaddy River. In response to the monsoons, the oceanic flow of surface waters in the Andaman Sea changes direction yearly two times with a cyclonic flow in spring and summer and anti-cyclonic flow for the rest of the year (Potemra et al., 1991). Current winds during SW monsoon drive the surface ocean eastward transferring the turbid Irrawaddy discharge from the river's mouths.

The Irrawaddy continental shelf and the Gulf of Martaban are covered by a modern inner-shelf mud belt while the outer shelf is covered with relict sands and carbonates (Rodolfo, 1969; Rao et al., 2005). Because of the macro-tidal setting, the high suspended sediment concentration is a continual feature in the Gulf of Martaban and the Irrawaddy continental shelf (Ramaswamy et al., 2004). Most of the suspended sediment discharged by the Irrawaddy River is transported eastward and deposited in the Gulf of Martaban along with those brought by the Salween River. A smaller fraction is transported into the eastern BoB from October to December. Evidence of suspended sediment transport as bottom flows directly into the deep Andaman Sea via the Martaban Canyon is also seen (Ramaswamy et al., 2004). Sediments deposited on the south-eastern Andaman shelf could be derived from south Myanmar and the western Thailand (Rodolfo, 1969).

2.1.5 The Arabian Sea and the Indian Ocean

Arabian Sea (Fig. 2.6) is a unique biogeochemical marine body which is part of the northern Indian Ocean with an average depth of > 3500 m (Shetye et al., 1994) and land-locked from three sides. It has many characteristic features such as (i) the high salinity and warm waters near surface originating from the Red Sea and the Persian Gulf waters, (ii) the enormous primary productivity because of the high nutrients supply through upwellings during the southwest (summer) monsoon (Madhupratap et al., 1996) and deposition of mineral dust from the nearby arid land masses to the Arabian Sea surface waters, (iii) the presence of oxygen minimum zones (OMZ) in its intermediate waters resulting from high productivity in the region sustained by upwelling during monsoon. (iv) The Arabian Sea receives high amount of fresh water $(9 \times 10^{13} \text{ L})$ and terrestrial sediment flux (400 MT) from the Indus River (Schulz et al., 1998; Garzanti et al., 2005), in addition it also receives annually $\sim 8 \times 10^{13}$ L of fresh water and ~ 100 MT of sediments from the Western Ghats of India through the Narmada, Tapi, Mahi and several other rivers those drain into the Arabian Sea. (v) The central Arabian Sea receives most of the Aeolian dust from nearby the land-masses and desserts of Oman, Africa and western India (Sirocko and Sarnthein, 1989; Goswami et al., 2014) as well as it receives about 0.16 to 25.4 mm day⁻¹ rainfall (http://giovanni.gsfc.nasa.gov/giovanni/). (vi) The Arabian Sea consists of a variety of water masses namely Arabian Sea high saline surface waters (ASHSW) from surface to 200 m water depth, BoB surface waters (BoBSW) surface to 200 m water depth in the southern Arabian Sea, the Persian Gulf and the Red Sea waters from subsurface to 600 m water depth, the North Atlantic deep waters (NADW) at 2000 m water depth and below 2000 m water depth the Antarctica bottom waters (AABW) respectively (Rochford, 1964; Wyrtki, 1973; Shenoi et al., 1993; Dileep Kumar and Li, 1996; Goswami et la., 2014).

In the Arabian Sea, trade winds are dominant during moonsoon which cause significant hydrographic, physical, biological and chemical variations in the water masses. The wet and dry northeasterly winds blow during winter (November to February) from a high-pressure cell of the Tibetan Plateau, whereas, heating of the Tibetan Plateau in summer (June to September) reverses the pressure gradient leading to warm and moist southwesterly winds and precipitation maximum. Presently, the SW monsoon is much stronger than its northeastern counterpart (Nair et al., 1989).



Fig. 2.6: The samples location map (dark blue dots) along with the cruise track (SS 300, red line) in the Arabian Sea during summer (April-May) 2012.

2.2 Geology

Geology is one of the important factors controlling the sediment generation and dissolved phases. In order to understand the physical and chemical erosion in the drainage basin, it is important to know the geological units that are drained by the river system.

2.2.1 Godavari River Basin

The GRS flows into the BoB along with other major rivers such as the G-B, Mahanadi, Brahmani, Krishna, Cauvery, Nagavali and the other east flowing rivers. The Godavari River basin drains an area of 313,147 km² in the central and southern part of the Indian subcontinent. The basin area occupies major geological formations (Fig. 2.7) like Cretaceous Deccan volcanic and Rajahmundry Traps (48%), Archean granites and gneisses (39%), Precambrian and Gondwana sedimentary rocks (11%), and recent Alluvial cover (2%) (Biksham and Subramanian, 1988a, c; Biksham et al., 1991; Jha et al., 2009; Vuba et al., 2015). The major part of the Godavari mainstream and its tributaries such as the Purna, Pravara, Penganga and the Manjira flows through the Deccan basalt; whereas, two tributaries namely the Indravati and the Sabari, joins into the Godavari from the north, which do not drain the Deccan basalt. Both of them drains through the granites, gneisses, charnokites and khondalites rock (~85%) and Precambrian and Gondwana sedimentary rock (15%; Biksham and Subramanian, 1988a, c; Raman et al., 1995).

2.2.1.1 The Deccan Traps:

Basalts of the Deccan and Rajahmundhary (~65 Ma) trap (Fig. 2.7) occupy 48% of the Godavari River Basin and consist essentially tholeiitic lava flows (Das and Krishnaswami, 2007; Manikyamba et al., 2015; Schoene et al., 2015; Vuba et al., 2015 and references therein). In the western-most part of the basin where the river originates, the traps have a thickness of about 3,500 m and gradually decreasing to ~200 m towards north and southeast (Das and Krishnaswami, 2007; Keller et al., 2012; Schoene et al., 2015). The rocks are often vesicular with secondary fillings of calcite, quartz, and zeolites. Olivine,

Plagioclase and augite are important major mineral assemblages with accessory phases of calcite, quartz, glauconite, zeolites and apatite (Manikyamba et al., 2015; Vuba et al., 2015). The vesicular structure along with columnar joint patterns present in these basalts makes them favorable for physical and chemical weathering.

2.2.1.2 Rajahmundry Traps Basin (RTB):

The late Cretaceous-early Tertiary RTB (~64 Ma) of the Krishna-Godavari Basin extends ~60 km on either side of the Godavari River. The RTB has been considered as the eastward continuation of the Deccan Traps and consists of basaltic flows interbedded with sedimentary horizons and is contemporaneous with the Deccan Traps.



Fig. 2.7: The samples location map of the Godavari River system (GRS). The map shows the geological settings of the GRS. Sampling has been done in two consecutive monsoon periods of 2013 and 2014 and the red circles indicate sampling locations in the GRS. Blue lines are the rivers and the continuous black line indicates the basin boundary of the GRS.

Plagioclase and clinopyroxene are the major minerals present in these basalts with minor olivine and glass (Knight et al., 2003; Das and Krishnaswami, 2007; Manikyamba et al., 2015; Vuba et al., 2015).

2.2.1.3 Archean Lithologies:

Archean rocks form the basement for the entire Godavari valley and are represented by granitoids and gneiss of Dharwar (3.36-2.7 Ga) and Bastar Cratons (3.5-2.5 Ga), (Fig. 2.7; Sarkar and Saha, 1983; Jayananda et al., 2008, 2013a, b; Wani and Mondal, 2011). Lithologically granitoids comprise of pink and grey granites, gneiss, migmatites and banded ferruginous quartzites. Mineralogically they consist of quartz, feldspar and biotite as major minerals while garnet, amphibole and chlorite and epidote as accessory minerals (Biksham and Subramanian, 1988c; Sarin et al., 2002; Das and Krishnaswami, 2007; Vuba et al., 2015).

2.2.1.4 Precambrian and Gondwana Sedimentary rocks:

The Gondwana sediments (Fig. 2.7) of the Godavari basin consist of argillaceous sandstones with shales as interstratas. These sediments occur in the central part of the valley, flanked on either side by the Proterozoic sediments. The Proterozoic sediments are in turn, flanked by the Archean basement rocks. The southwestern Proterozoic sediments of the Godavari basin consist of Pakhal sediments, basal conglomerates, dolomites, orthoquartzites, shales and sandstones. In the GRS, Deccan basalts dominate the geology of the upstream catchment; while granites, gneisses and sedimentary rocks (sandstones, quartzites and shales) are predominant in the lower catchment.

2.2.2 Geology of the Mahanadi and the Brahmani River basins

The Mahanadi and the Brahmani River basins are mainly composed of the Precambrian rocks of Singhbhum and Bastar cratons, Eastern Ghat khondalites, charnockites, leptynites, granite-gneissic complex of Chotanagpur terrain etc. The limestones, sandstones, coal and shales of the Gondwanas and the coastal tracts which are constituted by the recent deltaic alluvium of the river with littoral deposits. The Mahanadi River basin is covered with different lithologies viz. 34% of granite suite, 7% of khondalite suite, 15% of charnockite suite, 17% of limestone, shale of Lower Gondwana, 22% of sandstone, shale of Upper Gondwana and 5% of coastal alluvium throughout the basin. A part of the richest mineral belt of the sub-continent consisting of Fe ore, coal, limestone, dolomite, bauxite, Pb and Cu deposits also exists within the basin (Chakrapani and Subramanian, 1993; Konhauser et al., 1997; Sundaray et al., 2009; Khansa Zaidi et al., 2014).

2.2.2.1 Granite-Gneissic complex of Chotanagpur terrain

Chotanagpur Granite Gneiss complex (CGGC; 1.87-0.93 Ga) occupies a large area of about 10⁵ km² in the east-west trending subarcuate belt of the East Indian Shield (c. 500 km long in the east-west direction and 200 km in width). The Chhotanagpur plateau consists of Precambrian formations bound by the Gangetic Plain to the North. The Chhotanagpur gneiss is an E-W trending terrain consisting of a variety of gneisses and younger granites, narrow widespread but narrow belts of supracrustal enclaves, discontinuous boudin-type granulite belts and major parallel shear zones. The westernmost part of the CGGC and adjoining the Mesozoic Gondwana rocks of the Mahanadi Basin constitute the Ramanujganj-Tatapani (RT) sector. Palaeoproterozoic rocks of the Mahakoshal Group occur immediately west of the Gondwana Basin (Krishnan, 1982; Ramakrishnan and Vaidyanadhan, 2008; Sanyal and Sengupta, 2012).

2.2.2.2 Precambrian Rocks of Singhbhum and Bastar craton

The Odisha begins with a view of the craton that collectively form Peninsular India (Aravalli-Bundelkhand cratons, Singhbhum and Bastar cratons, the Western and Eastern Dharwar cratons and the Southern Granulite province; Fig. 2.8). The Bastar and Singhbhum cratons are separated from the Bundelkhand and Aravalli cratons (to the east) by the Narmada-Son lineament (Naqvi and Rogers, 1987; Goodwin, 1991). The Singhbhum Craton (also called the Singhbhum-Orissa craton; Fig. 2.8) stretches out along the eastern coast of India and borders the Mahanadi graben to the west the Narmada-Son lineament, and the Indo-Gangetic plain in the north. The Singhbhum nucleus is composed mainly of Archean granitoid batholiths, including the Singhbhum Granite complex. The batholiths are surrounded by several supracrustal rock complexes, the oldest of these is known as the Older Metamorphic Group (OMG). The OMG consists mainly of remnants in the form of micaceous schists, quartzites, calc-silicates, and para- and orthoamphibolites (Naqvi and Rogers, 1987). The OMG is intruded by the approximately 10^4 km² Singhbhum Granite complex consisting of granitic intrusions dated at ~3.5 Ga, 3.3 Ga, 3.1 Ga and ~0.9 Ga (Mishra et al., 1999; Mondal et al., 2007; Acharyya et al., 2008; Reddy et al., 2008). The two sections of Iron Ore group (IOG) with ages between 3.5 and 2.55 Ga are present in this basin (Eriksson et al., 2006; Mondal et al., 2007; Mukhopadhyay et al., 2008).

The Bastar Craton is bordered by the Mahanadi rift (in the northeast), the Eastern Ghats mobile belt (to the east), the Godavari rift (to the south), Deccan traps cover (to the west) and the Satpura mobile belt (in the north). The Precambrian units of the craton are represented by gneisses, granitoids, metasedimentary supracrustals and mafic dykes which together make up the bulk of the geology of the Bastar craton. The older supracrustals (Achaean to Paleoproterozoic) consisting of quartzites, phyllites, mica schists, banded hematite quartzites and agglomerates, belongs to Sausar, Sonakhan, Pakhal, Sukma, Bengpal, Bailadila, Nandgaon, Dongargarh, Khairagarh and Sakoli groups. Granitic gneisses that occur as large outcrops are the most prominent and ubiquitous rock types of the craton and form the basement of the Precambrian metasedimentary supracrustals especially in the north, northwest and southern part of the craton. Gneisses also occur as enclaves within the granitoids of younger age in the southern Bastar region. These gneisses with high alumina content and of trondhjemitic affinity have been dated at 3.5 Ga (Sarkar et al., 1993). Granitoid plutons of varying dimensions occur as intrusive into the



Fig. 2.8: The geological map of the Mahanadi and Brahmani Rivers. Red circles and triangles indicate sampling stations, while white and black dashed lines are the drainage basins of the Mahanadi and Brahmani Rivers respectively. Sampling has been done in September 2014.

gneisses and into the metasupracrustals throughout the craton. The granitoids form the second largest rock unit of the craton. Xenoliths of gneisses and metasupracrustals abundantly occur within the granitoids. The mafic dykes and dyke swarms cut across all the older units along predominantly NW-SE direction. The trondhjemitic granitic gneisses occurring as enclaves and the host granitoids that contain the gneisses have yielded U-Pb zircon ages of 3.0 and 2.4 Ga respectively (Sarkar et al., 1993); an age of 3.0 Ga has also been reported for the gneisses of granitic composition (Sarkar et al, 1990).

2.2.2.3 Gondwana Rocks

Gondwana Basins of India come up within the suture zones of the Precambrian cratonic blocks of Peninsular India along some linear belts. The Gondwana basins are linearly arranged along the present day river valleys viz. Koel-Damodar, Son-Mahanadi and Pranhita-Godavari. The sediments are mostly made up of clastics of glacial and glaciogene rocks at the base followed by coal measures and red beds at the top. The sedimentary sequence within the basin consists of a series of unconformity-bounded packages reaching an aggregate thickness of ~6000 m. The rocks are mildly deformed and weakly metamorphosed. Gondwana (300 to 180 Ma) Supergroup is subdivided into Lower Gondwana Group, characterized by Gangomopteris-Glossopteris flora and Mesozoic Upper Gondwana Group containing Dicroidium-Lepidopteris-Ptylophylum flora (Mukhopadhyay, et al., 2010).

2.2.3 Geology of the N-E Andaman catchment basin

The northern and eastern Andaman shelves receive sediments mainly through the Irrawaddy and Salween rivers. The Irrawaddy is the major river originating in the northern Myanmar with a catchment area of 4.1×10^5 km² and debouching in the Andaman Sea (Robinson et al., 2007). The Chindwin is its major tributary which joins it downstream Mandalay. The Salween River is much longer, ~2800 km with a catchment area ~2.7 × 10⁵ km² (Robinson et al., 2007). It originates in the Tibetan Plateau, flows through Yunnan Province of China, the Kayan and Mon States of Myanmar and debouches into the Gulf of Martaban in the Andaman Sea. Together the Irrawaddy and Salween provides ~550 MT sediments to the Andaman Sea. Smaller rivers such as the Kaladan, Naf, Lemro,



Fig. 2.9: The lithology map of the drainages of the Irrawaddy, the Salween and the Tanintharyi River basins falling in the Tibet, China, and the Myanmar, modified after Awasthi et al., (2014); Chapman et al., (2015).

Mayu etc are flowing through the western slope of the Indo-Burman ranges along the Rakhine coast supply sediments to the western shelf of Myanmar whereas smaller rivers of southern Myanmar, such as the Heinze, Ye, Tavoy, Tanintharyi and Lenya are flowing through the mountains of southern Myanmar and western Thailand contribute sediments to the eastern Andaman shelf.

The rivers bringing sediments to the Andaman Shelf drain various lithologies in their catchments. These rivers are draining through the major

lithologies, which are shown in Fig. 2.9. The Irrawaddy river flows in its upper reaches through the volcanics from a Cretaceous arc and sediments produced during the collision (Stephenson and Marshall, 1984; Maury et al., 2004; Najman et al., 2004; Szulc et al., 2006; Allen et al., 2008) and associated post-collision intrusive igneous rocks (Darbyshire and Swainbank, 1988). In the middle reaches, the Irrawaddy drains the Mogok Metamorphic Belt containing schists, gneisses, marble and migmatites (Fig. 2.9; Chapman et al., 2015). The catchment of the Irrawaddy River east of Mogok Metamorphic Belt comprises the older Palaeozoic sediments of the Asian Plate origin form the highlands of the Shan Plateau incorporating turbidites and carbonates. A significant part of the Irrawaddy basin lies in the Central Troughs (Eastern and Western Troughs, Fig. 2.9), which comprises late Cretaceous and younger sediments with granite-granodiorite intrusions and alkaline volcanoes. The Miocene granitic rocks extend from south of Mandalay towards western Thailand.

Many of the rivers along the Rakhine Coast and the western tributaries of the Irrawaddy such as the Chindwin River drain through the Indo-Burman hills comprising the Neogene and Paleogene sedimentary rocks, ophiolite and metamorphic rocks of Triassic to Cretaceous age (Fig. 2.9). The Indo-Burman hills contain Cretaceous-Cenozoic forearc flysh (Allen et al., 2008).

The Salween River drains the magmatic belt with Trans Himalayan batholith of the northern Lhasa block and Precambrian to Tertiary sedimentary, igneous and metamorphic rocks of the Shan Plateau/Sibumashu block (Fig. 2.9).

Rivers such as the Tanintharyi and the Tavoy draining the southern Myanmar and western Thailand flow through the Western and Central granitic Belts (Fig. 2.9; Nakapadungrat et al., 1984; Liew and Mc Culloch, 1985).



Flow chart 2.1: The field samples and the measured chemical compositions

41 | Page

2.3 FIELD SAMPLING

For the present work, water and sediment samples have been collected (in 2002, 2012, 2013 and 2014) from the Andaman shelf basin, Arabian Sea, Indian Ocean, Indian (the Godavari and the Mahanadi) river systems and its estuaries. I participated in the collection of water and sediment samples from the Arabian Sea, the Indian Ocean, the Godavari and the Mahanadi River basins and the East Indian estuaries in 2012, 2013 and 2014. The scientists from National institute of Oceanography, Goa collected sediment samples from the Andaman Shelf in 2002 and were made available to me for this study. Sampling details have been discussed below while sample locations are listed in Tables 2.2 to 2.7. The field samples and the measured chemical compositions in them are listed in flow chart 2.1.

2.3.1 The Arabian Sea and the Indian Ocean waters

The sampling has been done in the Arabian Sea and the Indian Ocean water columns in two consecutive years, 2012 and 2013 respectively (Table 2.2 and 2.3) to study the distribution of selected trace elements, tracking the various water masses and the global ocean circulation. The Hf and Nd concentrations, radiogenic isotope ratios, ¹⁷⁶Hf/¹⁷⁷Hf and ¹⁴³Nd/¹⁴⁴Nd were measured in the dissolved phase from the Arabian Sea and the Indian Ocean. The seawater sampling in the Arabian Sea onboard ORV Sagar Sampada during April-May, 2012 was done using the rosette equipped with general Conductivity-Temperature-Density (CTD) system containing 12 clean Niskin bottles with 12 L capacity. The Indian Ocean expedition was conducted onboard ORV Sagar Kanya during March-May, 2013 and sampling was done using new Sea-Bird clean rosette equipped CTD system with 24 clean containers of 12 L capacity similar to those being used in global GEOTRACES program (Fig. 2.10a, b).

In-situ measurements have been made for the general parameters like the salinity, potential temperature, potential density and dissolved oxygen (DO) using

calibrated CTD (Sea-Bird Electronics). Post collection, an aliquot of 1 L of water samples filtered using 0.2 μ m pore size Millipore filter in pre-cleaned (soaked in 3M HCl for 3-5 days and followed with Milli-Q (MQ) cleaning for 3-4 times) were stored in 1 L poly-propylene (pp) bottle onboard ORV SS 300 for trace elements analysis. In the SK 304 cruise, the water samples were filtered through 0.2 μ m Acropak cartridge filters in a HEPA filtered clean air van and were stored in pre-cleaned two 1 L pp bottles for trace metal analysis. The samples were acidified with quartz distilled (QD) HCl to bring the sample to pH ~2. These samples have been brought and stored at Physical Research Laboratory (PRL), Ahmedabad for the measurement of REEs and Hf concentrations (Goswami et al., 2014; GEOTRACES cookbook).

In both the expeditions, ~20 L seawaters for the analysis of Neodymium isotopic compositions (ϵ_{Nd}) and 60 to 100 L for the analysis of and Hafnium isotopic compositions (ϵ_{Hf}) from different depths in several water columns were collected (Fig. 2.10a-c).

2.3.2 River, estuary and rain water samples

Water and sediment samples have been collected during monsoon 2013 and 2014 from the Godavari, Mahanadi, and the Brahmani River basins and from four estuaries namely the Ganga (Hooghly), Mahanadi, Krishna and the Godavari to study weathering processes and geochemical behavior using major ion chemistry and TEIs. About 20-40 L of river waters were collected in pre-cleaned carboys. The turbid waters were allowed for several hours to settle down the suspended particulate matter (SPM). To analyze alkalinity, an aliquot of ~125 ml source water samples were stored before filtering them. The remaining water samples of ~20 L were filtered using the 0.2 μ m Acropak cartridge within 8 hrs of sampling time. For major ions analysis in the river and estuarine waters, a ~60 ml aliquot from each filtered sample was stored in a pre-cleaned pp bottles (soaked in MQ for one week). However, another ~1 L aliquot was taken in a pre-acid cleaned pp bottle, followed by acidification with QD HCl to bring the sample to pH ~2 and stored and shipped to the laboratory for the trace elements analysis. The remaining ~20 L of each filtered water samples were acidified using QD HCl to bring it to pH ~2 and were processed for the Nd isotope compositions at the sampling site and further purification and measurements were made at PRL, Ahmedabad. Rainwaters also sampled during the Mahanadi River sampling (during monsoon-2014) for the major ion chemistry and Sr isotope measurements. About 60-100 ml of rainwaters were collected in pre-cleaned pp bottles and transported to PRL.

Table 2.2: Sampling locations of the Arabian Sea onboard ORV Sagar Sampadaduring April-May, 2012.

Station	Date	Latitude °N	Longitude °E	Depth (m) of water column
SS 300-01	27/04/2012	9°26.626'	75°09.681'	2445.5
SS 300-02	30/04/2012	4°28.266'	69°27.476'	4353
SS 300-03	1/5/2012	3°00.005'	68°06.805'	3540
SS 300-04	3/5/2012	6°59.893'	70°59.690'	4070
SS 300-05	5/5/2012	11°00.036'	68°00.061'	4350
SS 300-06	6/5/2012	12°59.790'	68°59.932'	4175
SS 300-07	7/5/2012	14°59.768'	67°59.925'	3930
SS 300-08	8/5/2012	16°59.935'	67°59.814'	3553
SS 300-09	9/5/2012	19°00.245'	67°59.965'	3286
SS 300-10	10/5/2012	21°00.172'	67°59.976'	2674
SS 300-11	11/5/2012	19°59.958'	69°29.984'	158
SS 300-12	11/5/2012	19°59.981'	69°59.802'	80
SS 300-13	11/5/2012	19°59.855'	70°29.918'	78
SS 300-14	11/5/2012	19°59.905'	71°00.021'	70
SS 300-15	11/5/2012	20°00.155'	71°29.817'	36
SS 300-16	12/5/2012	18°29.788'	70°00.064'	1897
SS 300-17	13/5/2012	16°59.970'	71°29.883'	1434

		Latitude	Longitude	Depth (m) of water
Station	Date	°N/°S	°E	column
SK 304A-01	04/03/2013	13°42.343	73°15.774	800
SK 304A-02	06/03/2013	12°23.011	74°09.009	710
SK 304A-03	11/03/2013	09°52.015	75°32.016	760
SK 304A-04	17/03/2012	05°0.056	79°59.880	4327
SK 304A-05	23/03/2012	05°45.622	79°24.763	3408
SK 304A-06	27/03/2012	-0°31.738	86°33.570	4687
SK 304A-07	27/03/2012	-03°59.100	89°29.892	2020
SK 304A-08	02/04/2013	-11°9.648	97°59.165	5127
SK 304A-09	04/04/2013	-13°49.056	101°29.562	5072
SK 304A-10	06/04/2013	-16°1.544	104°27.766	5860
SK 304B-11	23/04/2013	-6°30.162	97°39.943	5401
SK 304B-12	24/04/2013	-5°28.051	97°22.397	4206
SK 304B-13	26/04/2013	-1°45.414	94°22.031	4798
SK 304B-14	28/04/2013	3°14.750	92°56.027	4511
SK 304B-15	29/04/2013	6°44.666	93°55.868	939
SK 304B-16	30/04/2013	8°20.016	95°0.137	2902
SK 304B-17	01/05/2013	11°0.252	95°0.179	3466
SK 304B-18	03/05/2013	12°35.022	93°52.127	2330
SK 304B-19	03/05/2013	12°55.190	93°5.843	328
SK 304B-20	03/05/2013	13°19.879	93°29.749	1889
SK 304B-21	04/05/2013	13°29.886	91°0.108	3023
SK 304B-22	03/05/2013	13°30.006	86°30.200	3213
SK 304B-23	08/05/2013	13°29.952	86°59.893	3439

Table 2.3: Sampling locations in the Indian Ocean onboard ORV Sagar Kanyaduring March-May, 2013.

Sample ID [#]	Latitude	Longitude	Water Depth $(m)^{\#}$
SK 175/3	17°29.47′	94°27.50′	49
SK 175/5	16°59.35′	94°20.78′	34
SK 175/10	16°29.73′	94°10.00′.	31
SK 175/14	16°00.03′	93°44.37′	160
SK 175/20	15°29.95′	94°00.03′	33
SK 175/22	15°30.83′	94°30.33′	37
SK 175/24	15°16.12′	94°44.65′	35
SK 175/26	15°00.39′	94°15.21′	66
SK 175/27	14°59.67′	94°00.13′	70

SK 175/32	14°29.88′	94°45.00′	93
SK 175/34	14°44.98′	94°59.88′	60
SK 175/36	15°14.88′	95°00.22′	32
SK 175/39	15°14.98′	95°15.16′	25
SK 175/41	14°44.84′	95°29.74′	95
SK 175/44	15°15.00′	95°45.23′	35
SK 175/45	15°30.32′	95°45.30′	16
SK 175/46	15°15.00′	95°59.64′	20
SK 175/47	15°15.03′	96°14.61′	19
SK 175/48	15°15.65′	96°29.81′	22
SK 175/49	15°15.29′	96°45.14′	22
SK 175/50	15°14.85′	96°59.65′	20
SK 175/51	15°14.55′	97°15.03′	20
SK 175/52	15°00.69′	97°15.03′	28
SK 175/54	14°59.37′	96°44.76′	27
SK 175/55	15°00.04′	96°29.74′	31
SK 175/57	15°00.03′	95°59.98′	68
SK 175/66	14°30.40′	96°29.73′	97
SK 175/69	15°30.50′	96°07.50′	16
SK 175/70	15°45.03′	96°09.57′	10
SK 175/71	15°39.03′	96°34.58′	11
SK 175/72	15°30.29′	96°40.31′	14
SK 175/76	14°30.13′	95°30.01′	90
SK 175/79	14°00.04′	97°30.14′	57
SK 175/80	14°14.99′	97°30.11′	50
SK 175/83	14°15.09′	96°45.46′	90
SK 175/87	14°15.11′	95°45.12′	165
SK 175/94	14°15.28′	94°00.07′	670
SK 175/96	14°00.83′	94°29.29′	550
SK 175/100	13°46.98′	95°52.00′	818
SK 175/103	13°45.06′	96°29.63′	138
SK 175/108	13°45.04′	97°45.13′	46
SK 175/115	13°00.10′	96°34.59′	245
SK 175/118	13°00.43′	98°29.85′	83
SK 175/120	12°30.47′	97°30.01′	80
SK 175/123	12°15.24′	96°59.84′	175
SK 175/129	12°00.25′	96°29.98′	1060
Salween River suspended matter	16°32.00′	97°37.10′	
Salween River bed-load	16°32.05′	97°37.20′	
Yangon River suspended matter	16°52.50′	96°05.45′	

Ramaswamy et al., (2008), provided more details of sampling in the northern Andaman basin.

Sample ID	River/Tributary	Date	Latitude	Longitude	pН	Temperature °C	Sample
Godavari Main	stream (GM)						
GDV-13/01	GM	28/08/2013	19°55'54.9"	73°31'03.2"	7.06	22.9	W
GDV-13/03	"	29/08/2013	19°37'22.9"	75°00'50.9"	7.21	26.1	W
GDV-13/04	"	29/08/2013	19°29'24.5"	75°22'33.0"	7.10	28.3	W
GDV-13/06	"	29/08/2013	19°08'41.7"	77°19'04.4"	6.90	27.8	w, s
GDV-13/07	"	30/08/2013	18°51'50.8"	77°57'29.1"	7.08	28.8	w, s
GDV-13/10	"	31/08/2013	18°57'56.55"	78°20'41.48"	7.12	28.8	W
GDV-13/12	"	31/08/2013	18°53'55.24"	79°09'14.14"	7.51	33.3	w, s
GDV-13/14	"	010/9/2013	18°48'58.62"	79°54'32.95"	7.35	29.1	w, s
GDV-13/16	"	01/09/2013	17°39'54.95"	80°52'39.79"	7.53	29.5	w, s
GDV-13/17	"	02/09/2013	17°00'16.00"	81°45'51.44"	7.60	29.6	w, s
GGV_14/01	"	15/09/2014	18°49'01.4"	79°54'33.9"	7.53	31.0	W
GDV-14/02_A	"	15/09/2014	17°40'06.2"	80°52'35.0"	7.30	29.0	W
GDV-14/02 _B	"	18/09/2014	17°40'02.6"	80°52'35.3"	7.71	30.3	W
GDV-14/05	"	18/09/2014	17°00'21.9"	81°45'51.1"	7.50	30.2	W
Godavari Tribu	ıtaries						
GDV-13/02	Pravara	28/08/2013	19°33'19.1"	74°55'26.5"	7.30	27.5	W
GDV-13/05	Purna river	29/08/2013	19°10'45.7"	77°00'50.6"	7.05	29.0	w, s
GDV-13/08	Manjira	30/08/2013	18°48'50.8"	77°52'55.0"	7.23	30.0	w, s
GDV-13/09	Peddavagu	31/08/2013	18°49'14.97"	78°26'19.39"	7.42	28.1	w, s
GDV-13/11	Kaddam	31/08/2013	19°06'27.25"	78°46'46.98"	7.48	30.5	W
GDV-13/13	Pranahita	31/08/2013	18°51'38.79"	79°57'23.50"	7.50	29.5	w, s
GDV-13/15	Sabari	01/09/2014	17°34'23.28"	81°15'28.36"	7.45	30.1	w, s
GDV-14/03	Indravati	17/09/2014	18°50'57.8"	80°20'58.2"	7.30	27.9	w, s
GDV-14/04	Indravati	17/09/2014	19°00'51.8"	81°11'23.3"	7.40	29.4	w, s

Table 2.5: Sampling details of the Godavari River System

w: water sample; s: sediment sample

Sample ID	River/Tributary	Date	Latitude	Longitude	pН	Temperature °C	Cond. (µS)
Mahanadi Main	nstream (MM)						
MND-14/01	MM	4/9/2014	21° 38' 21.84"	82° 23' 51.36"	6.8	27.1	70.6
MND-14/03	"	4/9/2014	21° 43' 51.96"	82° 33' 47.52"	6.9	25.7	97.4
MND-14/05	"	4/9/2014	21° 42' 57.59"	82° 35' 48.48"	6.9	26.5	85.7
MND-14/07	"	4/9/2014	21° 43' 27.48"	82° 47' 19.32"	6.7	26.1	99.0
MND-14/09	"	3/9/2014	21° 40' 40.8"	83° 17' 05.64"	7.5	27.8	107.3
MND-14/11	"	5/9/2014	21° 01' 26.4"	83° 48' 51.84"	6.8	26.6	75.0
MND-14/13	"	5/9/2014	20° 51' 45.72"	83° 54' 7.92"	6.7	26.8	95.0
MND-14/15	"	5/9/2014	20° 51' 34.92"	84° 18' 36.36"	6.8	25.1	42.0
Mahanadi Trib	utaries						
MND-14/02	Seonath	4/9/2014	21° 42' 46.8"	82° 21' 30.6"	6.9	27.8	151.2
MND-14/04	Jonk	4/9/2014	21° 39' 47.88"	82° 31' 44.04"	6.8	26.7	102.0
MND-14/06	Hasdeo	4/9/2014	21° 44' 52.44"	82° 43' 56.64"	6.1	26.2	118.4
MND-14/08	Mand	3/9/2014	21° 42' 49.32"	83° 15' 20.88"	7.4	27.4	169.0
MND-14/10	Ib	3/9/2014	21° 56' 28.68"	84° 01' 11.64"	7.0	27.2	59.5
MND-14/12	Ong	5/9/2014	20° 53' 51.36"	83° 48' 53.63"	6.0	26.9	101.0
MND-14/14	Tel	5/9/2014	20° 49' 42.59"	83° 54' 34.56"	6.8	26.0	77.8
Brahmani Mair	nstream						
BMN-14/01	Brahmani	5/9/2014	21° 50' 2.76"	84° 54' 13.68"	6.7	28.1	52.5
BMN-14/04	Brahmani	6/9/2014	22° 14' 14.28"	84° 47' 52.44"	6.7	28.7	67.1
Brahmani Trib	utaries						
BMN-14/02	Koel	6/9/2014	22° 16' 34.68"	84° 53' 58.56"	7.0	28.2	86.0
BMN-14/03	Sankha	6/9/2014	22° 14' 54.24"	84° 47' 16.25"	6.9	28.7	71.4
RW-14/01	Near Hasdeo	4/9/2014			5.8	23.8	6.1
RW-14/02	Near Shivanadh	4/9/2014			6.4	25.7	7.0
RW-14/03	At MND-14-11	5/9/2014			5.0	24.9	6.0

Table 2.6: The details of the Mahanadi and Brahmani River water samples

RW: Rainwater

Sample Id	Code	Latitude	Longitude	Date	Salinity	Temp.	pН	DO
Hooghly estuary								μM
BR10 35	G-1	22° 20'	87° 37'	26/08/2010	0.0		-	-
Hooghly-13/02	G-2	22° 12' 40.68"	88° 3' 55.44"	21/07/2013	0.35	-	-	-
Hooghly-13/01	G-3	22° 12' 26.28"	88° 4' 1.20"	21/07/2013	0.43	-	-	-
SM-24-13/01	G-4	22° 01.140'	88° 04.965'	22/07/2013	3.8	-	7.70	131
SM-24-13/02	G-5	21° 58.930'	88° 02.706'	22/07/2013	4.8	-	7.77	132
SM-24-13/03	G-6	21° 56.327'	88° 01.293'	22/07/2013	6.5	-	7.77	139
SM-24-13/04	G-7	21° 54.630'	88° 00.585'	22/07/2013	7.8	-	7.93	127
SM-24-13/05	G-8	21° 52.940'	87° 59.747'	23/07/2013	9.7	-	7.78	133
SM-24-13/06	G-9	21° 49.980'	87° 58.685'	23/07/2013	11.3	-	7.86	128
SM-24-13/07	G-10	21° 47.497'	87° 57.865'	23/07/2013	13.8	-	7.76	128, 132 ®
SM-24-13/08	G-11	21° 46.859'	87° 57.920'	23/07/2013	18.6	-	7.93	130
SM-24-13/09	G-12	21° 45.244'	87° 58.414'	23/07/2013	21.3	-	7.90	131
SM-24-13/10	G-13	21° 37.870'	88° 01.967'	23/07/2013	23.3	-	7.88	127
SM-24-13/11	G-14	21° 18.677'	88° 11.687'	23/07/2013	19.1	-	8.00	130
SM-24-13/12	G-15	20° 35.993'	87° 52.428'	23/07/2013	29.4	-	8.02	122
Mahanadi estuary	7							
MND-13/01	M-1	20°17'40.88"	86°41'52.20"	24/07/2013	0.0	-	7.88	-
MND-13/02	M-2	20°17'35.95"	86°42'21.38"	24/07/2013	0.1	-	7.99	-
MND-13/03	M-3	20°17'35.81"	86°42'24.63"	24/07/2013	0.2	-	7.95	-
MND-13/04	M-4	20°17'35.81"	86°42'28.64"	24/07/2013	0.4	-	7.92	-
MND-13/05	M-5	20°17'41.09"	86°42'46.26"	24/07/2013	2.8	-	7.83	-
MND-13/06	M-6	20°17'39.42"	86°42'43.00"	24/07/2013	23.7	-	8.14	-

 Table 2.7: Sampling details of the East Indian Estuaries
MND-13/07	M-7	20°15.026'	86°53.778'	24/07/2013	26.0	-	8.11	-
MND-13/08_Sur	M-8	20°19.336'	87°07.905'	24/07/2013	26.4	-	8.18	-
MND-13/08_35m	M-8	20°19.336'	87°07.905'	24/07/2013	-	-	8.02	-
MND-13/09_Sur	M-9	20°23.111'	87°23.046'	24/07/2013	32.4	-	-	-
MND-13/09_35m	M-9	20°23.111'	87°23.046'	24/07/2013	-	-	8.16	-
Krishna estuary								
KR-13/01	K-1	16°01'51.0"	80°52'28.5"	26/08/2013	0.0	29.4	8.49	-
KR-13/02	K-2	15°50'24.8"	80°52'04.0"	26/08/2013	0.5	29.4	8.49	-
KR-13/03	K-3	15°46'09.5"	80°50'29.3"	26/08/2013	1.9	29.5	8.44	-
KR-13/04	K-4	15°45'37.8"	80°50'14.0"	26/08/2013	2.7	29.3	8.42	-
KR-13/05	K-5	15°45'20.2"	80°50'08.8"	26/08/2013	4.0	29.8	8.41	-
KR-13/06	K-6	15°45'19.6"	80°50'06.7"	26/08/2013	5.1	29.8	8.39	-
KR-13/07	K-7	15°44'47.1"	80°49'56.5"	26/08/2013	6.9	30.3	8.40	-
KR-13/11	K-11	15°43'48.8"	80°49'48.8"	26/08/2013	10.3	31.0	8.39	-
KR-13/10	K-10	15°43'23.3"	80°49'50.9"	26/08/2013	14.6	31.2	8.37	-
KR-13/09	K-9	15°43'27.3"	80°49'50.0"	26/08/2013	18.1	31.1	8.37	-
KR-13/08	K-8	15°43'33.0"	80°49'49.9"	26/08/2013	30.2	30.7	8.27	-
Godavari Estuary								
GDV-13/18	G-1	16°43'17.40"	82°12'33.48"	2/9/2013	0	28.9	8.11	-
GDV-13/19	G-2	16°46'35.40"	82°21'36.72"	2/9/2013	1.6	28.6	8.11	-
GDV-13/20	G-3	16°46'50.16"	82°21'46.80"	2/9/2013	2.8	28.4	8.15	-
GDV-13/21	G-4	16°47'20.76"	82°22'45.12"	2/9/2013	5.1	28.5	8.23	-
GDV-13/22	G-5	16°47'23.28"	82°22'56.28"	2/9/2013	6.4	28.6	8.25	-
GDV-13/23	G-6	16°47'16.44"	82°23'50.64"	2/9/2013	10	28.5	8.25	-
GDV-13/24	G-7	16°47'18.24"	82°24'10.80"	2/9/2013	12.2	28.5	8.26	-
GDV-13/25	G-8	16°47'10.80"	82°24'58.32"	2/9/2013	15	28.3	8.31	-

-: Not measured and the data of BR10 35 sample used from Chatterjee, 2013.



Fig. 2.10 a. The sea and river waters sampling systematics onboard ORV Sagar Sampada, (SS-300) in the Arabian Sea expedition during April-May, 2012 and the Godavari and Mahanadi River sampling.



Fig. 2.10 b: The sampling using new Sea-Bird clean rosette equipped CTD system of 24 clean containers with 12 L capacity onboard ORV Sagar Kanya, Indian Ocean expedition during March-May, 2013 and their processing in the laboratory under clean environment.



Fig. 2.10 c: The pictures 'A-D' shows the purification processes of Nd-Hf isotopic compositions from the sea/river waters. The picture 'E' shows the purification processes of REEs and Hf concentrations using Nobias PA-1 chelate resin. All the processes have been made under clean environment (class 100 flow bench in class 10000 clean lab).

2.3.3 Sediment samples

The sediment samples analyzed in the present thesis are from the Andaman Shelf region (Table 4, Fig. 2.5), the GR systems and some of the suspended particulate matters (SPM) from the GR basin and the Ganga (Hooghly) estuary.

2.3.3.1 Sediment samples from the Andaman Shelf region and Irrawaddy River Basin

The surface sediments from the Andaman shelf were sampled by scientists from NIO, Goa onboard ORV Sagar Kanya during April-May, 2002 (Table 2.4, Fig. 2.5) to study their possible sources and assessing the factors impacting their delivery, dispersion and deposition in the shelf region. Details of sampling are reported in Ramaswamy et al. (2008).

2.3.3.2 Sediment samples from the Godavari River basins

Sediment samples of the GRS have been collected from the same locations along with water samples during monsoon 2013 and 2014 as discussed in section 2.1.1. The more details of the sampling period and locations are listed in Table 2.5 and shown in Fig. 2.2. The sediment samples were collected from the river bank. A few of the sediment samples have been collected from the middle of the river near low water discharge locations. The sediment samples (0.5 to 1 kg) were packed in polythene zip-lock bags and have been shipped to the laboratory.

2.3.3.3 Suspended Particulate Matters

The SPM have been collected from the Ganga estuary and the GRS during Monsoon 2013. These were collected from ~20 L water by decanting the supernatant waters from each sample after allowing them to settle for ~10-24 hrs and brought to the laboratory (PRL, Ahmedabad). In the laboratory, the SPMs from estuaries have been cleaned with de-ionized (MQ) water to remove sea-salt. Care was taken not to lose any SPM during washing. These SPMs were dried in an oven at 50 °C and then stored in pre-cleaned PP containers for the various analyses.

2.4 Analytical methods

As part of my thesis work, chemical separation and measurement protocols for Hafnium isotope (ε_{Hf}) composition of seawater samples have been

established for the first time in our laboratory. However, I employed the protocols and the analytical methods for other tracers such as Nd and Sr isotopic compositions in waters and sediments and elemental geochemistry followed in our laboratory (Singh et al., 1998; Rahaman et al., 2011; Goswami et al., 2014). The Hf chemistry and measurement protocols are presented first followed by Sr and Nd isotope chemistry, elemental chemistry in both the waters and sediment samples. The reagents used for processing the samples during collection and chemistry are enlisted in Table 2.9 along with their purity. The detailed applied methodology for seawater samples analysis of selected TEIs is given in Flow chart 2.2.

Table 2.8: Reagents used for the chemical processing of the samples collect during this study.

Acid	Product/Grade	Purification	Usage
Milli-Q water	18.2 MΩ		Chromatography
		Quartz/Teflon	Chromatography &
HCl	32%, p.a.	distilled	sample dissolution
			Chromatography &
HNO ₃	65%, p.a.	Teflon distilled	sample dissolution
			Chromatography &
HF	40%, Merck,	suprapure	sample dissolution
			Iron co-
NH ₃ Sol.	25%, Merck,	suprapure	precipitation
			Fe-extraction,
Di ethyl ether	> 99%, Merck	Back extraction	cleaning of FeCl ₃
$FeCl_3 \times 6H_2O$	> 99.99%, Merck,	Back extraction	Co- precipitation
Glacial Acetic	100%, Fisher		
Acid	Scientific	Back extraction	Chromatography



Flow chart 2.2: The methodology for seawater samples analysis

2.4.1 Sample collection and onboard procedures for Hf in water samples

For Hf isotope measurement, ~100 L of surface and ~60 L of sub-surface, deep and bottom seawaters were collected. Onboard ORV SS300, the samples collection have been carried out with Niskin bottles mounted on a regular rosette equipped with a CTD instrument from the surface to bottom water depths at each station. The samples were filtered ($< 0.45 \mu m$) within 12 hrs of collection and have been acidified to pH ~2 with quartz distilled HCl. Onboard ORV SK 304, ~60-100 L samples have been collected in the Indian Ocean water column using Teflon coated Niskin X 12 L bottles mounted on clean rosette and filtered using Acropack cartridge $(0.2 \ \mu\text{m})$ for the analysis of Hf isotopic ratios. To quantify the Hf concentration, about 2 L of each sample aliquots were separated and shipped to the laboratory. However, to analyze Hf isotope compositions, in the rest of the ~60-100 L of seawaters, nearly 3 mg of iron (Fe) per liter water sample, in the form of pre-cleaned dissolved Fe-chloride (FeCl₃, ~100 mg ml⁻¹ of Fe) was added to the samples and allowed for 24 hrs to get proper homogenization. This was followed by addition of ammonia solution (25%, Merck suprapure) to bring pH ~8 in order to co-precipitate the dissolved trace metals (i.e. Nd and Hf) with FeOOH. The supernatant of each sample has been discarded and the residual FeOOH precipitates were transferred into acid pre-cleaned 2L narrow mouth PPbottles for further analysis at PRL, Ahmedabad (Rickli et al., 2009, 2010, 2014; Zimmermann et al., 2009a, b; Stichel et al., 2012).

2.4.1.1 Procedures for Hf separation and measurement of its isotope composition

In the laboratory, the FeOOH precipitates centrifuged for 15 minutes at 3500 rpm to decant the remaining supernatant. The precipitates were rinsed 3-4 times with Milli-Q water (18.2 M Ω) followed by centrifugation to wash out the major ions. The samples were transferred from centrifuge tubes to 50 ml Teflon beakers using 6M HCl (TD). Fe was removed from the solution in order not to exceed the resin capacity during the ion chromatographic separation processes.

Excesses Fe has been extracted by adding a suitable amount of pre-cleaned diethyl ether to the samples using acid pre-cleaned Teflon separating funnel. In this process, the sample becomes pale yellow indicating the removal of the majority of iron from the solution. The samples have been carefully collected in Teflon beakers and dried till a jelly-like precipitate is formed. These precipitates allowed to dissolve using 0.5-1.0 ml of HF (Merck, suprapure) and evaporated and redigested using 1.5 ml of aqua-regia (HNO₃: HCl::1:3) followed by another evaporation.

To purify the Hf from the seawater samples, the entire chromatographic techniques have been listed in Table 2.9. The samples have been purified following the combination of three-column chemistry modified by Zimmermann et al. (2009a, b). Each sample has been loaded in 6 ml 1M HCl + 0.05M HF onto columns with 7.8 ml of AG 50W-X8 resin and eluted with 6 ml 1M HCl + 0.05M HF. After rejecting 8 ml of 6M HCl, REE eluted with 40 ml of 6M HCl. The Hf elutes were evaporated and re-dissolved in 4M HF to be loaded onto an anion column with 1 ml of AG 1-X8 resin. The columns were washed with 12 ml 4M HF, and then Hf was eluted with 6 ml 6M HCl + 1M HF. The Hf cut was dried completely and re-dissolved in 1 ml of 2M HCl + 0.1M HF. A final column with 0.7 ml of Eichrom Ln-Spec resin was used to separate Hf from Zr, as well as from any remaining Fe, Ti, Mg, Ca, Br, Cl, Lu, and Yb. The column has been washed with 14 ml of 2M HCl + 0.1M HF, and Hf was eluted using 20 ml 2M HCl + 0.1M HF. The final calibration curves for Hf purification shown in Fig. 2.11 (Patchett and Tatsumoto, 1980; Rickli et al., 2009, 2010, 2014; Zimmermann et al., 2009a, b; Stichel et al., 2012). The total yield after the precipitation and chemical separation procedure of Hf is 70-75%. The purified fractions of Hf have been measured using MC-ICP-MS in 0.4M HNO₃ + 0.1M HF. Hf isotope measurements have been carried out using MC-ICP-MS in static multi collection mode. The parameters of MC-ICP-MS were described in Table 2.10. These isotopic data have been corrected for instrumental fractionation by normalizing the Hf data with the stable isotope ratio 179 Hf/ 177 Hf = 0.7325. During the course of this study, the Hf isotope measurements of standards were also carried out. The average ${}^{176}\text{Hf}/{}^{177}\text{Hf}$ ratio of standard JMC 475 during these measurements 0.282145 \pm 0.000007; (2 σ , n = 15; Fig. 2.12) were found consistent with their recommended values. However, the internal precision of the samples analysis for ϵ_{Hf} from seawaters is 0.42 \pm 0.2 ϵ_{Hf} . Due to the lower concentrations in the surface samples, a few of them are measured with a large uncertainty which is 1.25 \pm 0.40 of ϵ_{Hf} . The total procedural blank for the Hf isotopic composition was 60-80 pg.

Table 2.9: Applied chromatographic treatment of the samples to extract and purify Hf from seawaters.

Stage	Acid	volume
Pre-cleaning	6M HCl + 0.03M HF	20 ml
Change acid	M.Q.	Full
Pre-cleaning and Conditioning	1M HCl + 0.05M HF	2 + 2 + 2 ml
Load and Collect Hf	1M HCl + 0.05M HF	6 ml
Collect Hf	1M HCl + 0.05M HF	6 ml
Elution	1M HCl + 0.05M HF	2 ml
Elute Fe, Ba	6M HCl	6 ml
Collect REE	6M HCl	40 ml
Elution	6M HCl + 0.03M HF	Full
Clean	M.Q.	Full
Pass and store	1M HCl + 0.05M HF	20

A: Hf and REE separation on 7.8 ml of AG 50W-X8 (200-400 MESH)

B: Hf separation on 1 ml of AG1-X8 (200-400 MESH)

Stage	Acid	volume
Pre-cleaning	6M HCl + 1M HF	5 ml
Change acid	M.Q	5ml * 2
Pre-conditioning	4M HF	1 ml *2
Loading	4M HF	1 ml
Fixing	4M HF	1 ml
Elute (Fe, Ti, Mo, Ca, Br, Sr & Cl)	4M HF	12 ml
Collect Hf	6M HCl + 1M HF	6 ml

Stage	Acid	volume
Pre-cleaning	6M HCl + 1M HF	5 ml
Change acid	M.Q	5ml * 2
Pre-conditioning	2M HCl +0.1M HF	1 ml *2
Loading	2M HCl +0.1M HF	1 ml
Fixing	2M HCl +0.1M HF	1 ml
Elute	2M HCl +0.1M HF	14 ml
Collect of Hf	2M HCl +0.1M HF	20 ml
Clean	6M HCl + 1M HF	FULL * 2
Wash MQ	M.Q	FULL * 2
Store	1M HCl	FULL

C: Hf purification on 1 ml of Eichrom LN-Spec (100-150µm)



Fig. 2.11: The final purification of Hf using Ln-Spec resin from seawaters fractions. All REEs are remained at background level indicating Hf has been purified without any interference from Yb and Lu.

MC-ICPMS	parameters	Desolvating devi	ce (Aridus)
Detection system:	9 Faraday collectors	Sweep Gas Flow:	4.93 ml min ⁻¹
FV:	1.07×10^{-3} mbar	Nitrogen Gas Flow:	009 ml min ⁻¹
HV:	2.85×10 ⁻⁷ mbar	Temperature:	110 °C
IGP:	2.55×10^{-8} mbar	Desolvating device ((Apex)
Cool gas flow rate (Ar):	14.5 L min ⁻¹	Temperature:	110 °C
Auxiliary gas (Ar):	$1 \mathrm{Lmin}^{-1}$		
Sample Gas (Ar):	0.971 L min ⁻¹		
Acceleration voltage:	10 kV		
Argon Max:	5.80 bar		
RF power:	1200 W		
RF reflected power:	< 3 W		
Interface cones:	Zet cone		
Spray chamber :	Aridus for Hf isotopes		
	Apex for Nd isotopes		
	SIS for both Sr and Nd		
Sample uptake rate:	100 ml min ⁻¹		
Integration time :	8.33 sec		
Instrument Resolution:	450 (low)		
Signal collection time:	10-15 min (6-10 blocks	X 10 cycles)	
Baseline determination:	ca. 100 sec on peak in 2	2% HNO3	

 Table 2.10: The parameters of MC-ICPMS during Hf isotopes measurements in seawaters

SIS: Stable Introduction System

2.4.1.2 Hf concentration measurements in seawaters using isotope dilution method

Concentration of Hf in seawater was measured using isotope dilution (ID) technique. A known amount of seawater, 1000 ml was spiked with known amount of Hf spike and after proper equilibration; Hf was separated from seawater using Nobias PA1 resin. This procedure is established for the first time in our laboratory and which has been detailed in the following section.

Using measured mixed ratios (R_m) of couple of Hf isotopes, the concentrations of Hf in natural waters were quantified by the ID equation (Faure, 1977):

$$[Hf]_{Sample} = [Hf]_{Spike} \frac{W_{Nat}}{W_{spike}} \frac{M_{Spike}}{M_{Sample}} \frac{Ab2_{Spike}}{Ab2_{Nat}} \frac{\left(\frac{Ab1_{Spike}}{Ab2_{Spike}} - R_m\right)}{\left(R_m - \frac{Ab1_{Nat}}{Ab2_{Nat}}\right)} \qquad \dots \dots 2.1$$

where W_{Nat}: Natural atomic weight,

W_{Spike}: Spike atomic weight,

M_{Sample}: Weight of sample in g

M_{Spike}: Weight of spike added to the sample in g,

 $Ab1_{Nat}$, $Ab2_{Nat}$, $Ab1_{Spike}$, $Ab2_{Spike}$: The respective abundances in natural and spike of isotopes 1 and 2.

R_m: Mass bias corrected ratio of isotopr1/isotope2 in the sample/spike mix measured using Q-ICPMS.

The ideal amount of Hf enriched spike to be added to the natural sample is taken based on the ideal R_m which is determined by:

$$R_{m-ideal} = \sqrt{\frac{Ab1_{Spike}}{Ab2_{Spike}}} \frac{Ab1_{Nat}}{Ab2_{Nat}} \qquad \dots 2.2$$

2.4.1.3 Preparation and Calibration of Hf spike

To quantify Hf concentration from natural waters, an enriched Hf isotope spike (¹⁷⁸Hf) has been procured from Oak Ridge National Laboratory (ORNL), Tennessee, USA, dissolved and diluted suitably and calibrated on Q-ICPMS. The Hf concentrations in the ocean waters measured using 'isotope dilution' method followed by Zimmermann et al., (2009a, b). The abundances of Hf isotopes of the natural sample and spike are given in Table 2.11 and the calibrated Hf results are listed in Table 2.12. We prepared the tracer solution of the Hf spike from its oxide salt obtained from the ORNL, Tennessee. The precise weight of oxide salts of Hf has been taken in acid pre-cleaned new Teflon vials. The accurately weighed oxide salt of Hf has been digested using 4 ml of concentrated Hydrofluoric acid (HF; SEASTAR) overnight at 110 °C.



Fig. 2.12: The variations in ¹⁷⁶Hf/¹⁷⁷Hf of standard JMC 475 measured during measurements of seawaters on MC-ICPMS. The measured values are consistent with their recommended values.

Hf (amu)	Natural (%)	Spike (%)
174	0.16	0.02
176	5.26	0.27
177	18.60	1.55
178	27.28	94.66
179	13.62	1.84
180	35.08	1.68

Table 2.11 Atomic abundances of Hf isotopes in the natural sample and the spike

Table 2.12: Results of calibrated Hf Spike

	Wt. of Hf Std	Wt. of Hf spike	Hf spike conc.
	(g)	(g)	$(pg g^{-1})$
Hf Spike Cal 1	1.00559	2.02166	779.90
Hf Spike Cal 2	1.01589	2.02227	779.95
Hf Spike Cal 3	1.01192	2.16633	811.23
		Mean	790.36
		STDEV	18
		RSD (%)	1.0

The 178-Hf spike solution transferred into the acid pre-cleaned and pre-weighed new PTFE 500 ml bottle and diluted to about 500 g of 0.4M HNO₃ solution. The spike has been calibrated using Certipur [®] Hf ICP standard. A primary stock solution of Hf spike with concentration 8.747 μ g g⁻¹ enriched in ¹⁷⁸Hf (recently calibrated) was diluted appropriately according to seawater concentration level using 0.4M HNO₃. The diluted Hf spike solution calibrated using Certipur [®] Hf ICP standard. Three sets of pre-weighted aliquots of spike and ICP standard solution were mixed and equilibrated and measured on Q-ICP-MS. The calibrated concentration of Hf spike is given in Table 2.12.

Pre-weighed ~1 kg of seawater samples have been spiked with the known weight of ¹⁷⁸Hf enriched spike and homogenized for five days. 5.0 ± 0.5 ml of freshly prepared 3.7M Ammonium acetate buffer solution (Mixture of Suprapure Ammonia solution, Acetic acid and Milli-Q water-NH₄Ac) with a pH 9.4 \pm 0.2 has been added to the spiked sample to obtain pH 4.60 \pm 0.2 of the sample. Once

the sample attains this pH value, samples were passed through the Nobias chelate PA1 resin loaded in a micro-column procured from Global FIAS to extract Hf from seawaters by eluting it using 2.0 ml of 0.4M HNO₃ (modified after Biller and Bruland, 2012; Hatje et al., 2014). The detailed Hf (for concentrations) extraction processes from seawater are given in Table 2.13. The eluted Hf was diluted to 3.0 ml with 0.4M HNO₃ and measured on Q-ICPMS.

The reproducibility of the Hf concentration measurements has been evaluated by measuring the samples in duplicates. The results expressed as absolute error (%) and coefficient of variation is given in Table 2.14. However, the external precision of the samples analysis for concentrations of Hf from seawaters is $7 \pm 4\%$ (Table 2.14). The absolute error (%) and CV (%) were calculated using the equations below.

$$Abs.Error(\%) = Abs\left(\left(\frac{d_i}{X_i}\right) \times 100\right) \qquad \dots 2.3$$
$$CV(\%) = \left(\frac{1}{2n} \Sigma \left(\frac{d_i}{X_i}\right)^2\right)^{1/2} \times 100 \qquad \dots 2.4$$

Table 2.13: Hf purification on 2.0 ml of the Nobias chelate PA1 resin loaded in micro-column

Stage	Acid	volume
Pre-cleaning	3 M HNO ₃	50 ml
Pre-cleaning	0.1 M HNO ₃	10 ml
Pre-washing	0.05M NH ₄ -Ac (pH 4.5± 0.2)	10 ml
Pre-washing	1 M HNO3	20 ml
Pre-conditioning	$0.05M \text{ NH}_4\text{-Ac} \text{ (pH } 4.5 \pm 0.2 \text{)}$	10 ml
Sample loading	pH 4.5± 0.2	1000 ml
Matrix	0.05M NH ₄ -Ac (pH 4.5± 0.2)	10 ml
Hf collection	1 M HNO3	2.0 ml
Rejection	1 M HNO3	10 ml
Cleaning	3 M HNO3	50 ml
Store	0.1 M HNO3	25 ml

Table 2.14: The repeat measurements of Hf concentrations in seawater and their

 Coefficient of Variation (CV %)

Sample ID	Hf, pmol kg ⁻¹	Abs. Error (%)
SS 300-05/210 m_1	0.52	1 /
SS 300-05/210 m_2	0.53	1.4
SS 300-09/5 m_1	0.36	14.2
SS 300-09/5 m_2	0.41	14.2
SK 304A-06/05 m_1	0.22	22 T
SK 304A-06/05 m_2	0.18	22.1
SK 304A-10/1000 m_1	0.66	13.8
SK 304A-10/1000 m_2	0.57	15.0
SK 304B-13/300 m_1	0.41	9.3
SK 304B-13/300 m_2	0.37	2.2
SK 304B-13/300 m_3	0.35	5.5
SK 304B-13/300 m_4	0.37	1.6
SK 304B-17/600 m_1	0.4	1.6
SK 304B-17/600 m_2	0.41	0.6
SK 304B-17/600 m_3	0.41	1.0
SK 304B-21/2850 m_1	0.68	77
SK 304B-21/2850 m_2	0.74	1.1
Average abs. error (%)		6.8
CV (%)		4.4

2.4.2 Sample collection and onboard pre-concentration procedures for Nd isotopes and its concentration in water samples

About 20 L of seawater samples have been collected for the measurements of Nd isotopic composition at several depths of the water column. The collection has been carried out with the Niskin bottles mounted on a rosette equipped with a CTD instrument. The samples were filtered (0.2 μ m) within 8 hrs from the sample collection and acidified with QD HCl to obtain pH ~2. An aliquot of 500 mL of sample was separated to quantify the REEs concentration. Nearly 3 mg iron (Fe) per liter, in the form of pre-cleaned dissolved Fe-chloride (FeCl₃, ~30 mg ml⁻¹ of Fe) was added to the samples and allowed for ~20 hrs to get proper homogenization. This has been followed by the addition of ammonia solution (25%, Merck suprapure) to bring pH ~8 in order to co-precipitate the dissolved trace metals with FeOOH (i.e. Nd). The supernatants of all the samples have been discarded and the residual FeOOH precipitates have been collected using Whatman filter papers, followed by re-dissolution using required amount of 6M (QD) HCl and stored in acid pre-cleaned 60 mL PP bottles and transported to the home laboratory, PRL, Ahmedabad (Amakawa et al., 2000; Rickli et al., 2009, 2010, 2014; Zimmermann et al., 2009a, b; Stichel et al., 2012; Goswami et al., 2014).

2.4.2.1 Procedures for Nd isotopes measurement in the seawater samples

The pre-concentrated Nd samples have been replaced from 60 ml pp bottles to the acid pre-cleaned Teflon beakers and allowed overnight to dry completely at 100 °C under class 10000 clean lab environment. In the next step, the samples have been treated with HF: HNO₃: HCl acid mixture and dried. Pure Nd has been extracted by following chromatographic techniques with two column chemistry modified by Goswami et al. (2014) and references therein (Table. 2.16A-C). The dried Nd samples with Fe were re-dissolved in 4-6 ml of 6M HCl and loaded into columns with 7 ml of AG1-X8 resin to remove excess Iron and eluted REE with 6 ml of 6M HCl. The eluted REE was allowed to dry completely and was re-dissolved in 1 ml of 2M HCl and loaded onto the cationic column, AG50W-X8 resin. Major elements like Ca, K, Mg and Rb, Sr etc. were rejected with 45 ml of 2M HCl and 6ml of 6M HCl and after that purified REE were collected with 9 ml of 6M HCl. The REE cut kept for dryness and re-dissolved in 0.5 ml of 0.16M HCl and loaded into the Ln-Spec resin and purified Nd was eluted with 4 ml of 0.27M HCl. The purification steps for Nd are shown in Fig 2.13a, b. The purified Nd cuts were evaporated to dryness and re-dissolved in 0.4M HNO₃ and measured on MC-ICP-MS. The chemical yield of the entire preconcentration and separation procedures for Nd were 80-55%. Nd isotopes were measured using MC-ICP-MS in static multi collection mode. The measurement parameters of MC-ICP-MS are listed in Table 2.10. In the case of Nd isotopes analysis, the Aridus spray chamber has been replaced with the Apex introduction system to introduce the sample into the MC-ICP-MS. These isotopic data have been corrected for instrumental fractionation by normalizing the Nd data with the stable isotope ratio 146 Nd/ 144 Nd (= 0.7219). During the course of this study, Nd isotopic measurements of standards also have been carried out. The average 143 Nd/ 144 Nd ratio of standard JMC 321 during these measurements 0.511076 \pm 0.000018; $(2\sigma, n = 16; Fig. 2.14)$ were found consistent with their recommended values. At many measurement schedules, ¹⁴³Nd/¹⁴⁴Nd of JMC 321 was measured lower side compared to the reported value (143 Nd/ 144 Nd = 0.511123 ± 0.000012, Fig. 2.14; Barrat and Nesbitt, 1996) and hence the ¹⁴³Nd/¹⁴⁴Nd in samples have been corrected by normalization to the reported ¹⁴³Nd/¹⁴⁴Nd of JMC 321. The internal precision of the samples analysis for ε_{Nd} from seawaters is 0.35 \pm 0.2 ε_{Nd} . Due to the lower concentrations in the surface samples, a few of them are measured with a large uncertainty which is 0.80 ± 0.25 The total procedural blank for the Nd isotopic composition was 125 pg.

Table 2.15: Applied chromatographic treatment of the samples to extract and purify of Nd from seawaters.

Stage	Acid	volume
Pre-cleaning	6M HCl	20 ml
Change acid	M.Q	$5 \text{ ml} \times 2$
Pre-conditioning	6M HCl	$2 \text{ ml} \times 2$
Loading	6M HCl	2 ml
Collect REE	6M HCl	2 ml×2

	A.	REE separation	on 7.0 ml	of AG 1-X8	(200-400 MESI
--	----	-----------------------	-----------	------------	---------------

Stage	Acid	volume
Conditioning	2M HCl	5 ml * 2
Loading	2M HCl	1 ml
Fixing	2M HCl	1 ml * 2
Washing	2M HCl	8 ml
Collection(Rb)	2M HCl	7 ml
Rejection	2M HCl	13 ml
Collection(Sr)	2M HCl	7 ml
Rejection	2M HCl	7 ml
HCl Normal	ity changed here	to 6N
Rejection	6M HCl	6 ml
Collection (REEs)	6M HCl	9 ml
Clean	6M HCl/M.Q.	Full
Store	M.Q	Full

B. REE separation on 3.5 ml of AG 50W-X8 (200-400 MESH)

C. REE separation on 1.25 ml of Ln-Spec. resin (100-150 $\mu m)$

Stage	Acid	volume
Conditioning	0.16M HCl	5ml
Loading	0.16M HCl	0.5ml
Fixing	0.16M HCl	0.5ml
Washing/Rejection	0.16M HCl	15ml
HCl Normali	ty changed here to	0.27N
Rejection	0.27M HCl	1 ml
Collection(Nd)	0.27M HCl	4ml
Clean	6.0M HCl	Full
Store	M.Q.	Full



Fig. 2.13 a: The separation resolution of Rb, Sr and REE in seawaters using 16 ml of cation exchange resin AG 50W- X8 (200-400 MESH). The plot suggests all the REEs were separated from major elements.



Fig. 2.13 b: The purification of Nd from REE fraction in seawaters using 1.25 ml of Ln-Spec resin (50-100 MESH). The curves indicate no Sm (isobaric) interference on Nd.

2.4.2.2 REE's concentration measurements using isotope dilution method

We have prepared the individual tracer solutions of the REEs (La, Ce, Nd, Sm, Eu, Gd, Dy, Er, Yb and Lu) spikes from their oxide salts (Table 2.16) obtained from ORNL, Tennessee. The precise weights of oxide salts of the REEs have been taken in acid pre-cleaned new Teflon vials. Except for La, Ce, all the other oxide salts of the REEs have been dissolved immediately in 4ml of 10% TD HNO₃ (Roddick et al., 1992; Sullivan and Roddick, 1992). Even though, for the better dissolution of their oxide salts were digested overnight at 110 °C. The oxide salt of La has been digested using the mixture of concentrated 4 and 2 ml of HNO₃ and H₂O₂ respectively overnight at 110 °C. However, the Ce oxide salt digested in 5 ml of 25% of H₂SO₄ (SEASTAR) in the overnight at 110 °C. All these individual REE spike solutions transferred into the acid pre-cleaned and pre-weighed new PTFE 500 ml bottles and diluted to about 500 g of the solution of each. All these spikes have been calibrated using appropriate ICP single element standards.



Fig. 2.14: The variations in 143 Nd/ 144 Nd of standard JMC 321 during these measurements of seawaters on MC-ICPMS.

S. No.	REE Oxides	Batch	Isotope	Form	Net wt. (mg)	Order No.	Source
1	Lanthanum	134701	La-138	La_2O_3	5.9	67-0116	ORNL
2	Cerium	156891	Ce-142	CeO_2	6.1		"
3	Neodymium	161691	Nd-145	Nd_2O_3	5.8		"
4	Samarium	167392	Sm-149	Sm_2O_3	5.8		"
5	Europium	151990	Eu-153	Eu_2O_3	5.8	"	"
6	Gadolinium	109391	Gd-155	Gd_2O_3	5.8		"
7	Dysprosium	171491	Dy-161	Dy_2O_3	5.7		"
8	Erbium	173491	Er-167	Er_2O_3	5.7	"	"
9	Ytterbium	196001	Yb-171	Yb_2O_3	5.7		"
10	Lutetium	TRAC 4-09-0	Lu-176	Lu_2O_3	5.7	"	"

Table 2.16: The basic details of REE spikes procured from ORNL

ORNL: Oka Ridge National Laboratory

2.4.2.3 Preparation and calibration of REE spikes

The quantification of REEs from natural waters was done using isotope dilution technique as mentioned in section 2.4.1. b. To quantify REEs of natural waters, I have been prepared mixed spike of eight enriched REE isotope (Ce, Nd, Sm, Eu, Gd, Dy, Er and Yb; Rousseau et al., 2013, 2015; Hatje et al., 2014) using calibrated individual primary spikes and again calibrated on Q-ICPMS. The REEs quantification in natural waters has been done by addition of known quantities of the above mentioned mixed spike to the samples (Rousseau et al., 2013, 2015; Hatje et al., 2014). The mixture of eight spikes, multispike, has been calibrated using eq. 1 and 2 (more details in the above section 2.4.1. b). The abundances, ratios and atomic weights of natural and spike details of REE isotopes were shown in Table 2.17. The calibrated concentrations of REE in mixed spike were given in Table 2.18.

Pre-weighed seawater sample aliquots of 50-60g have been spiked with known concentrations of 'multispike'. Samples were allowed to homogenize for ~24 hrs. In the next step, 3.5 ± 0.5 ml of freshly prepared 3.7M Ammonium acetate buffer solution (Mixture of Suprapure Ammonia solution, Acetic acid, and Milli-Q water-NH₄Ac) with a pH 9.4 \pm 0.2 was added to the sample to obtain pH

 4.7 ± 0.2 . Once the sample pH attains to 4.7 ± 0.2 , the REEs have been extracted using 0.27µl of Nobias chelate PA1 resin. The detailed extraction processes have been listed in Table 2.19. The REE elutes have been diluted to 4.5 ml of 0.4 M HNO₃ and measured on Q-ICPMS (*Thermo X-series II*; Hatje et al., 2014). The concentrations of eight REEs have been determined using isotope dilution techniques by adding mixed spike and concentration of the rest of the REEs have been determined using standard calibration method followed by efficiency correction for chemistry using spiked REEs recovery.

Table 2.17: The REEs isotopes, abundances, isotope ratios and atomic weights of natural and spike solutions

	I-1	I-2	Ab ¹ _N	Ab ² _N	Ab ¹ _s	Ab ² _s	W _N	Ws	Ab_N^1/Ab_N^2	Ab ¹ _S /Ab ² _S
				%	, D					
Ce	142	140	11.11	88.45	92.85	7.15	140.12	141.77	0.126	12.986
Nd	145	146	8.29	17.18	91.73	3.67	144.24	144.90	0.483	24.995
Sm	149	147	13.82	14.99	97.67	0.37	150.37	148.93	0.922	263.26
Eu	153	151	52.19	47.81	98.79	1.21	151.96	152.90	1.092	81.645
Gd	155	157	14.80	15.65	94.31	1.02	157.25	155.03	0.946	92.461
Dy	161	163	18.89	24.90	95.75	0.89	162.50	161.01	0.759	107.58
Er	167	166	22.95	33.60	91.77	2.81	167.26	166.98	0.683	32.658
Yb	171	172	14.28	21.83	95.07	2.61	173.04	171.03	0.654	36.425

I-1: Isotope-1; I-2: Isotope-2; Ab: Abundance, W_N and W_S : atomic weight of the natural and Spike element, Subscripts N and S refer to natural and spike respectively.

 Table 2.18: Results of calibrated concentrations in mixed REE Spike for seawaters

REE	REE (pg g ⁻¹), n=3	RSD (%)
Ce	125.5	1.0
Nd	118.9	1.6
Sm	90.0	3.6
Eu	97.0	2.2
Gd	51.4	3.4
Dy	116.3	2.4
Er	163.8	0.9
Yb	75.8	1.6

Stage	Acid	volume
Pre-cleaning	3 M HNO ₃	10 ml
Pre-cleaning	0.1 M HNO ₃	2.0 ml
Pre-washing	0.05M NH ₄ -Ac (pH 4.7± 0.2)	1.0 ml
Pre-washing	1 M HNO3	8.0 ml
Pre-conditioning	$0.05M \text{ NH}_4\text{-Ac} \text{ (pH } 4.7 \pm 0.2)$	2.0 ml
Sample loading	pH 4.7± 0.2	50 - 60 ml
Matrix	$0.05M \text{ NH}_4\text{-Ac} \text{ (pH } 4.7 \pm 0.2)$	2.0 ml
REE collection	1 M HNO3	0.5 ml
Rejection	1 M HNO3	2.0 ml
Cleaning	3 M HNO3	10 ml
Pass & Store	0.1 M HNO3	2.0 ml

Table 2.19: REE's purification on 0.27 μl of the Nobias Chelate PA1 resin

Accuracy of REEs measurements were further ascertained by analyzing samples collected at location (#SS 300-07) during our cruise in the Arabian Sea which is very close to the Station #1605 for which REEs data are available in German and Elderfield (1990). REEs measured in samples collected from the station, SS 300-07 agree quite well with those reported for station #1605 (Fig. 2.15; German and Elderfield, 1990) indicating a good accuracy of these measurements.





Fig. 2.15: The REE concentrations measurements in the present study (#SS 300-07) along with those reported for nearby station #1605 (German and Elderfield, 1990) and #0802 (Goswami et al., 2014). Both results agree quite well except Gd.

2.4.3 River and estuary waters chemistry

2.4.3.1 Sr-Nd isotope measurements in the river and estuarine waters

The sampling processes in river basins and estuaries are discussed in the section 2.3.2. In the laboratory, all the samples have been processed for trace elements and isotopes (TEIs) in class 10000 clean environments under class 100 laminar flow bench. The Nd isotope compositions in dissolved phase of river basins were determined following the same procedure outlined for the seawater in 2.4.2 (Table 2.13a-c; Fig. 2.12a, b). The purified Nd fraction has been measured on MC-ICP-MS (Neptune Plus from Thermo Fisher).

The Sr isotope compositions and its concentrations in river and estuarine waters were determined after the extraction of Sr from samples using Sr-Spec resin (Rai and Singh, 2007; Rahaman and Singh, 2012). Pre-weighed ~1-50 g of acidified estuarine and freshwater samples have been spiked with enriched ⁸⁷Sr spike and allowed ~24 hrs for a better homogenization. The homogenized samples were dried completely at 100°C, followed by addition of 1-2 ml of aqua regia (1:3 HNO_3 : HCl) and evaporated at 100°C to remove any organic matter of them. Finally, the samples have been re-dissolved in 0.5ml of 3M HNO₃, which was loaded on the Sr-Spec resin. 3M HNO₃ has been used to remove the major elements Ca, Mg and Rb etc. Finally, the purified Sr has been eluted using 6.0 ml of M.Q. (18.2 M Ω) water. The Sr elutes have been dried completely, re-dissolved and diluted using 0.4M HNO₃ for isotope and concentrations analysis on MC-ICP-MS. Measurement of Sr-Nd isotope compositions have been carried out using MC-ICP-MS in a static multi collection mode. These isotopic data were corrected for instrumental mass fractionation by normalizing the Sr and Nd isotopic data with 86 Sr/ 88 Sr (=0.1194) and 146 Nd/ 144 Nd (=0.7219) respectively.



Fig. 2.16: The variations in ⁸⁷Sr/⁸⁶Sr of standard NIST SRM 987 during these measurements of both river and marine waters and sediments on MC-ICPMS.

The Sr and Nd concentrations have been calculated using the isotope dilution technique. During the course of this study, the Sr and Nd isotopic measurement of standards also have been carried out. The average 87 Sr/ 86 Sr ratio of standard SRM 987 during these measurements 0.710324 ± 0.000014; (1 σ , n = 21, Fig. 2.16) and 143 Nd/ 144 Nd for JMC Nd 0.511711 ± 0.000027 (1 σ , n = 38, Fig. 2.17) were consistent with their recommended values. The total procedural blank of Sr (~30 pg, Table 2.20) and Nd (100 pg) for these analyses are found a few orders of magnitude lower than total Sr and Nd processed. The precision of the analysis has been checked using the repeat analysis of water samples for Sr concentration and its isotopic composition. The repeat analytical results have been listed in Table 2.20.



Fig. 2.17: The variations in ¹⁴³Nd/¹⁴⁴Nd of MERCK Nd standard during these measurements of seawaters on MC-ICPMS.

2.4.3.2 Trace elements analysis in river and estuarine waters

The chemical procedures to extract the REEs from river and estuarine waters were made on Nobias chelate PA1 resin (Rousseau et al., 2013; Hatje et al., 2014) following the same protocol used for the seawaters as discussed in the section 2.4.2. ii. The pre-weighed ~10 to 15g of samples from river waters and ~50 to 60g of estuarine waters have been spiked with calibrated and highly enriched mixed REE spike and allowed to homogenize for 24 hrs. REEs have been extracted using Nobias chelate PA1 resin at pH 4.7 \pm 0.2 and analyzed on Q-ICP-MS. The precession of the REEs analysis in river and estuarine waters were checked by repeating the samples analysis and their results were provided in Table 2.21 including the coefficient of variation (%).

The analysis of Mn in river and estuarine waters has been done on Q-ICP-MS. All the fresh river waters of < 1 salinity were measured on Q-ICP-MS without any dilution. However, the estuarine waters have been diluted and made their salinity ≤ 1 and quantified Mn concentration. In the course of Mn concentration analysis, to check the accuracy of the analysis, the certified reference material SLRS-4 was analyzed several times. The results of SLRS-4 measured in this study were given in Table 2.22. The measured Mn concentration of SLRS-4 was consistent with their certified values indicating the good accuracy of these measurements. During the course of these measurements, the blank was almost at ground levels for Mn.

Table 2.20: The repeat analysis results of Sr concentrations and its isotopic compositions in the river and estuarine waters.

Sample ID	⁸⁷ Sr/ ⁸⁶ Sr	Sr, µmol Kg ⁻¹
GDV-13-11	0.71681	2.01
GDV-13-11	0.71669	1.99
GDV-13-16	0.71421	1.36
GDV-13-16	0.71420	1.36
GDV-13-24	0.70939	30.34
GDV-13-24	0.70936	30.13
KR-13-10	0.70950	36.26
KR-13-10	0.70953	36.96
KR-13-08	0.70920	73.89
KR-13-08	0.70923	74.03
Hooghly-13-01	0.71829	2.04
Hooghly-13-01	0.71827	2.05
SM 24-13-06	0.70965	28.40
SM 24-13-06	0.70967	28.57
SM 24-13-11	0.70930	45.80
SM 24-13-11	0.70932	45.24
SM 24-13-14_35m	0.70924	77.03
SM 24-13-14_35m	0.70920	76.36
MND-13-06	0.70926	56.15
MND-13-06	0.70923	56.23
Pro. BLK (n=4)		~30 pg

2.4.3.3 Major ions and silicate measurements in river and estuary waters

The applied general methodology to quantify the major ions compositions in river waters has been derived from the previous studies (Singh et al., 2005; Rai and Singh, 2007). Temperature and pH (Table 2.5) of the river and estuary water samples were measured at the site using their respective probes (portable multi parameter-meter by WTW). The dissolved Na, K, Ca, Mg, Cl, SO₄ and NO₃ concentrations present in riverine and rain waters have been measured on Ion chromatography (Thermo Scientific, DIONEX ICS-5000 DC) from the filtered and un-acidified aliquot. The Dionex Ion Pac^{TM} CG16 and Dionex Ion Pac^{TM} AG23 Guard columns have been used for the analysis of cations and anions respectively. Both anion and cation analyses have been done simultaneously with the detection limit of 1 μ mol L⁻¹, Alkalinity (HCO₃) measurements were done using the acid titration using a *Metrohm[®] Auto-titrator* in the un-filtered and unacidified aliquot. The Si concentrations in the river and estuarine waters have been determined on ICP-AES. The precision of measurements for various anions and cations, determined based on repeat measurements, is better than 5%. The validity of measurements is checked with the reference standard SLRS-4 and other four published BR 10 series samples (Yeghicheyan et al., 2001; Chatterjee, 2013). It shows a good accuracy of the analysis. Table 2.22 and Table 2.23 show the repeat measurements of standards and samples showing the accuracy and precession of the analysis. The coefficient of variation (CV%, Table 2.23) is \leq 1.5% for individual measurements suggesting quite accurate measurements.

2.4.4 Sediments

The present study also deals with the sediments of the Andaman shelf basin and from peninsular rivers and estuaries namely the Ganga, Mahanadi, Krishna and the Godavari. These sediments have been investigated for geochemical and Sr-Nd isotopic compositions as proxies to study the source, geological settings, and chemical weathering intensity. A portion of the sediments (100-150g) were transferred into cleaned glass beakers and dried completely at 100 °C for 1-2 days. Once dried, they were allowed to cool in desiccators and stored in pre-cleaned plastic containers for further analysis (Singh et al., 2008).

Table 2.21: The repeat analysis of REEs concentrations (pmol kg⁻¹) and the Coefficient of Variation (CV %) of REEs in riverine and East Indian estuary waters

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
GDV-13/17	218.8	56.8	45.1	94.4	15.7	2.8	33.7	5.4	15.3	7.6	19.5	2.9	13.3	3.7
GDV-13/17	218.7	57.5	46.9	86.6	14.5	2.6	31.9	5.4	14.0	8.1	18.8	3.4	11.4	3.3
KR-13/05	21.6	38.1	7.8	37.3	8.8	1.9	23.7	2.1	16.3	4.0	23.6	2.6	16.3	2.5
KR-13/05	21.1	39.0	7.6	38.8	8.8	2.0	23.5	2.0	15.7	3.7	24.0	2.7	17.1	2.7
GDV-13/25	414.2	340.5	78.7	311.3	44.5	7.4	31.2	7.2	46.8	10.8	61.3	6.3	34.6	5.1
GDV-13/25	504.0	307.6	83.1	327.3	50.1	7.5	28.9	7.0	45.8	10.8	63.6	6.2	34.4	5.0
SM_24_13_07	22.5	17.3	5.5	27.9	7.4	1.4	25.4	2.1	16.8	4.5	28.9	3.1	20.8	3.0
SM_24_13_07	25.0	19.9	6.0	28.1	6.6	1.4	9.0	2.0	16.4	4.2	27.8	2.9	19.2	3.0
MND_14/01	389.4	400.6	88.7	332.0	50.7	6.6	403.8	5.6	29.8	5.2	31.8	2.9	19.9	2.7
MND_14/01	326.7	436.9	89.1	355.8	52.6	6.6	494.5	5.5	30.8	5.4	31.1	2.6	17.7	2.4
CV (%)	4.49	3.09	1.79	2.01	3.05	1.29	3.51	1.10	1.75	1.79	1.11	2.91	3.41	2.95

Table 2.22: The repeat measurement results of the major ions (μ mol L⁻¹), Si (μ mol L⁻¹) and Mn (μ g L⁻¹) of the river waters, standard seawater and Canadian River water standard (SLRS-4)

	Na	K	Ca	Mg	Cl	SO_4	NO ₃	HCO ₃	Si	Mn	
Measured											
Std. $SW^{\#}(2)$	-	-	-	-	-	-	-	2199.8		-	
SLRS-4 ^{\$} (4)	101.5	17.9	151.1	64.4	-	-	-	-	-	3.77	
BR1018 (4)	269	103	706	262	99	147	56	-	-	-	
BR1024 (2)	473	97	664	257	243	149	75	-	-	-	
BR1029 (2)	259	86	667	257	98	121	44	-	-	-	
BR10 32	-	-	-	-	-	-	-	-	120	-	
BR10 35	-	-	-	-	-	-	-	-	119	-	
			R	eporteo	1						
Std. SW								2210.54			
SLRS-4	104.4	17.4	154.7	65.8						3.53	
BR10 18	260	101	657	247	96	144	54				
BR10 24	473	96	626	248	254	146	72				
BR10 29	250	84	606	241	99	118	42				
BR10 32									124		
BR10 35									131		

Std. SW: Standard Seawater

-: not analyzed; **#:** Reference material for Oceanic CO₂ measurements, Batch-42; \$: Yeghicheyan et al., 2001; **BR series:** Chatterjee, 2013. The parenthesis value is the number of times measured/repeated throughout the present study.

ID	Na	K	Ca	Mg	Cl	SO ₄	NO ₃	ID	Alkalinity	ID	Si
GDV-13-01	216	48	226	46	126	47	17	GDV-13-05	3017	GDV-13-13	368
GDV-13-01	218	48	235	49	126	48	16	GDV-13-05	3255	GDV-13-13	359
GDV-13-07	1312	91	660	726	702	250	145	GDV-13-07	2916	GDV-13-16	324
GDV-13-07	1276	87	641	706	716	250	142	GDV-13-07	2790	GDV-13-16	311
GDV-13-15	300	35	264	137	176	24	31	GDV-13-12	2702	GDV-13-25	231
GDV-13-15	300	35	263	136	177	23	33	GDV-13-12	2765	GDV-13-25	218
GDV-13-18	482	48	599	307	222	76	55	GDV-13-14	2027	KR-13-08	51
GDV-13-18	490	49	599	311	235	80	56	GDV-13-14	2006	KR-13-08	50
GDV-13-20	36909	997	1653	3599	43109	2382	b.d.	GDV-13-16	1761	GDV-14-03	303
GDV-13-20	36836	998	1653	3569	41635	2297	b.d.	GDV-13-16	1617	GDV-14-05	299
GDV-13-24	164793	4047	4211	17731	199564	10022	b.d.	GDV-13-21	1593	GDV-14-03	253
GDV-13-24	161361	3972	4171	17268	204320	10140	b.d.	GDV-13-21	1656	GDV-14-05	251
KR-13-10	190416	4057	4539	19796	208401	10945	b.d.	KR-13-02	1750	RSD (%)	0.09
KR-13-10	190604	4036	4509	19855	203678	10715	b.d.	KR-13-02	1736		
Hooghly-02	3578	161	728	633	3291	341	b.d.	KR-13-06	1862		
Hooghly-02	3606	163	733	642	3332	346	b.d.	KR-13-06	1946		
SM-24-13-13-S	375943	10286	9740	32759	380496	22483	b.d.	KR-13-11	1638		
SM-24-13-13-S	380531	10474	9489	33623	375085	21594	b.d.	KR-13-11	1673		
MND-13-06	307407	6465	6835	34362	322901	20230	b.d.	MND-14-01	836		
MND-13-06	309787	6433	6792	34683	326874	20665	b.d.	MND-14-01	853		
MND-14-01	132	31	299	63	64	27	32	GDV-14-03	878		
MND-14-01	135	32	306	65	64	28	31	GDV-14-03	880		
MND-14-08	360	42	740	227	126	468	56				
MND-14-08	364	43	751	230	125	468	56				
CV (%)	0.5	0.7	0.6	1.0	0.8	0.9	1.2		1.5		1.2

Table 2.23: The results of repeated major ions of the river waters analyzed during this study. CV (%) also given. All the repeat measurements and CV (%) indicates precise and accurate measurement.

b.d.: Below detection

2.4.4.1 Powdering

About 100 g of sediment samples were powdered using a disc mill with agate containers. These powders were sieved to $< 100 \ \mu m$ using nylon sieves. The sediment portions $> 100 \ \mu m$ were repeatedly powdered using the same processes till the entire samples are brought to $< 100 \ \mu m$. Care was taken to avoid any contamination between the sample to sample during the complete process. These powders were stored in new and pre-cleaned plastic containers and used for various geochemical and isotopic studies.

Table 2.24: The table shows the results of repeat analysis of all the sediment samples during this study.

Sample ID	¹⁴³ Nd/ ¹⁴⁴ Nd	8 _{Nd}	[Nd] µg g ⁻¹	⁸⁷ Sr/ ⁸⁶ Sr	[Sr] µg g ⁻¹
SK 175 / 47	0.512102	-10.45	15.7	0.72095	66
SK 175 / 47	0.512134	-9.83	15.3	0.72106	69
SK 175 / 52	0.511959	-13.25	12.9	0.72279	66
SK 175 / 52	0.511963	-13.17	13.3	0.72289	65
SK 175 / 72	0.512078	-10.92	13.0	0.72244	66
SK 175 / 72	0.512081	-10.87	13.8	0.72322	64
SK 175 / 103	0.511955	-13.32	16.6	0.72324	65
SK 175 / 103	0.511969	-13.05	17.7	0.72330	70
SR BL	0.511847	-15.43	20.5	0.73144	72
SR BL	0.511890	-14.59	19.3	0.73119	72
GDV-13-14	0.511340	-25.31	11.0	0.73521	159
GDV-13-14	0.511385	-24.45	10.9	0.73547	156
GDV-13-17 in Riv.	0.511236	-27.35	3.7	0.75528	133
GDV-13-17 In Riv.	0.511235	-27.37	3.9	0.75556	132
GDV-13-16 (SL)	0.511795	-16.45	13.8	0.72809	87
GDV-13-16 (SL)	0.511720	-17.90	13.2	0.72859	74
KR-13-02	0.511155	-28.93	2.7	0.76666	151
KR-13-02	0.511182	-28.41	2.8	0.76638	151
GDV-14-02	0.511513	-21.94	14.3	0.73636	130
GDV-14-02	0.511611	-20.03	13.1	0.73645	128
SM 24-13-10 (SL)	0.511785	-16.63	16.2	0.75762	45
SM 24-13-10 (SL)	0.511784	-16.65	16.4	0.75810	41

Riv.: River; SL: suspended load; SR BL: Salween River, Bed load

2.4.4.2 Geochemical and isotopic Analysis

The elemental and Sr-Nd isotopic compositions analysis of the sediment samples were carried out in their silicate fractions. For the same, samples were treated with 0.6M HCl and ultra-sonicated at 60 °C for 30 minutes to remove inorganic carbon (de-carbonation) and centrifuged at 3500 rpm for 30 minutes. The de-carbonation processes were repeated 2-3 times until no CO₂ bubbles were observed and any remaining acids were removed by rinsing with de-ionized (MQ) water for 3 times by centrifuge the samples at 3500 rpm. The supernatant was decanted without any sample loose and allowed to dry in the oven at 100 °C for 1-2 days. These sediments were re-powdered using agate mortar and pestle and ashed in the furnace at 600 °C for 6-8 hrs to oxidize organic matter. The obtained fractions, the silicate fractions, were stored in cleaned plastic containers.

2.4.4.3 Sr-Nd isotopes analysis

The analyses of Sr-Nd isotopic compositions were carried out in the silicate fractions. The pre-established analytical methodology of Physical Research Laboratory, India (Singh et al., 2008; Tripathy et al., 2011; Goswami et al., 2012) was followed for separation and measurement. The silicate fraction of the sample, together with known amount of ⁸⁴Sr and ¹⁵⁰Nd spikes was digested completely using HNO₃-HF-HCl acids. Pure fractions of Sr and Nd were separated from the solution using conventional column chromatography (Table 2.15B, C; Fig. 2.13a, b) (Singh et al., 2008). Measurements of Sr-Nd isotopes were carried out using MC-ICP-MS in static multi collection mode. These isotopic data were corrected for instrumental fractionation by normalizing the Sr and Nd isotopic data with 86 Sr/ 88 Sr (=0.1194) and 146 Nd/ 144 Nd (=0.7219) respectively. The Sr and Nd concentrations were calculated using isotope dilution. During the course of this study, Sr and Nd isotopic measurement of standards were also carried out. The average ⁸⁷Sr/⁸⁶Sr ratio of standard SRM 987 during these measurements 0.710332 \pm 0.000014; (1 $\sigma,$ n =21; Fig. 2.16) and $^{143}\text{Nd}/^{144}\text{Nd}$ for MERCK Nd 0.511711 \pm 0.000027; (1 σ , n = 38; Fig. 2.17) were found
consistent with their recommended values. However, the measured standard ratios were either lower or higher than the reported values, those set of samples were normalized with the help of the reported ratios. The total procedural blank for Sr (~1.8 ng) and Nd (100 pg) for these analyses are found few orders of magnitude lower than total Sr and Nd processed. The precision of the analysis was checked by repeating the sample measurements and the overall repeated results during this study are reported in Table 2.24.

Sample ID	Na	K	Ca	Mg	Al	Fe	Ti	Mn
				wt. %				$\mu g g^{-1}$
	0.70	2.34	1.93	1.56	7.01	2.17	0.39	420
SCo-1 ^{\$} (n=2)	± 0.06	± 0.02	± 0.01	± 0.04	± 0.06	± 0.18	± 0.03	± 29
	0.67	2.30	1.87	1.64	7.25	2.27	0.38	410
SCo-1®	± 0.04	± 0.07	± 0.14	± 0.11	± 0.11	$\pm .08$	± 0.04	± 30
SK175/24	1.05	1.05	0.73	0.85	3.92	2.44	0.26	231
SK175/24	1.05	0.97	0.69	0.78	3.88	2.56	0.24	248
SK175/41	0.56	1.67	0.22	1.24	9.97	4.28	0.54	303
SK175/41	0.56	1.66	0.21	1.18	9.86	3.98	0.49	325
SK175/51	0.56	1.32	0.21	0.78	6.75	4.39	0.50	403
SK175/51	0.59	1.43	0.20	0.85	7.06	4.63	0.54	368
SK175/83	0.41	1.33	0.17	0.53	5.28	4.88	0.39	212
SK175/83	0.38	1.34	0.16	0.57	5.26	5.00	0.36	194
GDV-13/07	0.83	0.54	2.62	1.31	4.11	8.41	2.56	846
GDV-13/07	0.97	0.56	3.59	2.57	6.22	11.63	2.37	777
GDV-13/17	0.76	2.10	1.05	0.59	3.63	1.60	0.24	16
GDV-13/17	0.78	2.15	1.08	0.60	3.73	1.67	0.24	13
Hooghly-13/02	0.67	2.28	0.66	1.81	7.47	5.63	0.50	179
Hooghly-13/02	0.67	2.36	0.61	1.94	7.83	5.78	0.51	215
SM-24-13/06	0.52	2.35	0.62	2.16	8.26	6.82	0.61	276
SM-24-13/06	0.50	2.26	0.57	2.03	8.19	7.38	0.58	260
SM-24-13/07	0.52	1.72	0.56	1.93	8.08	7.37	0.60	252
SM-24-13/07	0.50	1.56	0.53	1.70	7.39	7.05	0.63	269
CV (%)	2.1	2.0	4.5	7.8	4.9	4.0	3.9	3.1

Table 2.25: The table shows the results of repeat analyses of all the sediment samples during this study.

\$: measured; **®:** Certified

2.4.4 Major Elements chemistry

The geochemical analyses were made in the silicate fraction of sediments. About 250 mg of silicate fractions have been digested using MILESTONE microwave system by treating with HNO₃-HF-HCl acids in equal portions. The dissolved solutions were transferred into Teflon beakers and dried completely at 100 °C on a hot plate. These samples were re-digested using aqua regia (1:3; HNO3: HCl) solution. This processes repeated until the samples were digested properly and re-dissolved in 0.4M HNO₃. Abundances of major elements (e.g. Al, Ca, Mg, Fe, Mn, and Ti) in these solutions were measured using an ICP-AES (Jobin-Yvon, Ultima), whereas Na and K were measured using Flame-AAS (Perkin-Elmer). The results of major elements in rock standard (SCo-1) and repeat measurements of samples were given in Table 2.25. A few samples were analyzed in replicate to determine the precision of measurements; these replicate measurements show that the analytical reproducibility of the geochemical analysis is about 8%.

Chapter 3

Erosion and Weathering in the Peninsular Indian Rivers and Fluxes to the Bay of Bengal

3.1 Introduction

Rivers are the primary transporters of the dissolved and particulate materials eroded from continents to the global ocean. The chemical composition in river waters is primarily controlled by the chemical weathering of minerals of rock/sediments existing in the drainage basins, whereas, the physical erosion of rocks in the basin controls the abundance of the particulate matters in the rivers. The present chapter describes the impact of chemical weathering on the elemental budget and Sr-Nd isotope compositions of dissolved and particulate matters of the major peninsular rivers in India. It has been attained by measuring the chemical compositions and $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} of the dissolved and particulate components of the Godavari, Mahanadi and the Brahmani Rivers. The silicate weathering of the continents regulates the climate change over million year time scale. The chemical weathering of silicate minerals on continent enhances drawdown of atmospheric CO₂, which leads to neutralization of Earth's heat budget and influences climate change over the million year time scales (Berner et al., 1983; Raymo and Ruddiman, 1992; Ruddiman, 1997; Krishnaswami et al., 1999; Kump et al., 2000; Dessert et al., 2001; Amiotte-Suchet et al., 2003; Dessert et al., 2003; Huh, 2003; Das et al., 2005) that led to large number of studies on the chemical weathering of several global rivers (Sarin and Krishnaswami, 1984; Sarin et al., 1989, 1992; Krishnaswami et al., 1992, 1999; Palmer and Edmond, 1992; Probst et al., 1994; Edmond and Huh, 1997; Gaillardet et al., 1997; Galy and France-Lanord, 1999; Dessert et al., 2001; Dalai et al., 2002; Singh and France-Lanord, 2002; Bickle et al., 2003, 2005; Das et al., 2005; Singh et al., 2005, 2006; Rai and Singh, 2007; Rengarajan et al., 2009; Tripathy et al., 2011).

It is well recognized that the ⁸⁷Sr/⁸⁶Sr of the ocean has been gradually enhanced through the Cenozoic (DePaolo and Ingram, 1985; Palmer and Elderfield, 1985; Elderfield, 1986; Hess et al., 1986; Veizer, 1989; Richter et al., 1992) which has been attributed to the Himalayan orogeny followed by enhance weathering in its basin. Several studies have demonstrated that weathering of silicate minerals releases radiogenic Sr (Edmond, 1992; Krishnaswami and Singh,



1998; Dessert et al., 2001; Dalai et al., 2003; Bickle et al., 2005; Das et al., 2005; Rengarajan et al., 2009).

Fig. 3.1: The sampling location map of the Godavari, Mahanadi and the Brahmani River systems along with the geological settings of the basin. Sampling has been conducted in two consecutive monsoon periods of 2013 and 2014. Here, EGB refers Eastern Ghats Belt.

Several parameters such as basin lithology, runoff, rainfall, temperature, vegetation and relief regulate the rate and intensity of chemical weathering (Berner and Berner, 1996, 2012; Drever, 2005) and associated CO_2 consumption rates (CCR). The basin lithology plays a prominent role in chemical weathering

(Edmond and Huh, 1997). In general, basalts weather faster compared to the gneissic and/or granite rocks (Meybeck, 1987; Bluth and Kump, 1994; Amiotte-Suchet and Probst, 1995; Amiotte-Suchet et al., 2003). Studies carried out by Dessert et al., (2001) and Das et al., (2005) on weathering of the Deccan Trap basalts in the western Indian Rivers such as the Narmada, Tapi, Wainganga-Wardha and the Krishna suggest higher chemical weathering rates of basalts compared to other silicates. The estimated activation energy of basalts (~42 KJ mol⁻¹) based on a global data is lower compared to that derived for granites (~50-80 KJ mol⁻¹; White and Blum, 1995; White et al., 1999a, b; Dalai et al., 2002).

An effort has been made in this thesis to study the chemical weathering patterns and their controlling factors in the rivers draining the peninsular India having different lithologies such as basalts and gneisses. The primary objectives of this study are to construct (i) the chemical weathering rates of the Godavari, Mahanadi and the Brahmani River systems using major ion compositions of the respective river waters and their impact on global climate changes, (ii) the spatial and temporal variations of dissolved and particulate elemental abundances, Sr-Nd concentrations and ⁸⁷Sr/⁸⁶Sr, ε_{Nd} in these rivers and factors influencing their variations, and (iv) estimation of the dissolved and particulate chemical fluxes to the Bay of Bengal (BoB) and ultimately to the world oceans affecting their modern global oceanic budget.

3.2 Results

3.2.1 The dissolved chemical composition in the peninsular Indian River systems

The water and sediment samples were collected from a few of the peninsular Indian Rivers such as the Godavari, Mahanadi and the Brahmani and their tributaries during the monsoon period of 2013 and 2014. The majority of the water samples were collected from the middle of the rivers, whereas a few were collected near the bank of the rivers. The details of the sampling locations are listed earlier in Chapter-2 (Table 2.5; Fig. 3.1) and the pH and temperature of the waters were provided in Table 2.5. The concentrations of major ions, total dissolved solids (TDS), Sr, 87 Sr/ 86 Sr, 143 Nd/ 144 Nd ratios, ε_{Nd} and Calcite

Saturation Index (CSI) of the water samples are presented in Table 3.1. The concentrations of dissolved rare earth elements (REEs) are listed in Table 3.2. At few locations, bed load and suspended particulate matters (SPM) were also collected in the Godavari River System (GRS) to study their geochemical and isotopic behavior in the basin as well as to track their sources. The abundances of major elements (Na, K, Ca, Mg, Fe, Al, Mn and Ti), Sr and Nd and Sr-Nd isotopic compositions analyzed in the silicate fractions of the Godavari River sediments are listed in Table 3.3.

3.2.2 Primary observations in the peninsular Indian River systems

The physical parameters of the peninsular rivers are mentioned earlier in Chapter-2 (Table 2.1). The mean monthly water and sediment discharges of the Godavari and the Mahanadi River are shown in Fig. 3.2 (Bikshamaiah and Subramanian, 1980; Chakrapani and Subramanian, 1990; http://www.grdc.sr.unh. edu/). The majority of water and sediments of both the rivers are discharged during three months (July to September) of monsoon period. The pH of the GRS water samples collected during peak monsoon (August-September, 2013 and 2014) ranges between 7.06 and 7.60, with an average of 7.3 (\pm 0.2), suggesting moderately alkaline nature of most of the samples; whereas, the pH of the Mahanadi and the Brahmani River waters varied within the range of 5.0 to 7.5, with an average of 6.8 (\pm 0.3) pH, few of the samples are mildly acidic. Rainwater samples were also collected during the Mahanadi field trip, (September, 2014) which is also acidic in nature with an average pH of \sim 5.7. In the present study, the temperature of the GRS water samples ranged from 22.9 to 33.3 °C, lowest at head waters and maximum in intermediate and downstream reaches. Temperatures of waters of the Mahanadi and the Brahmani Rivers vary from 25.1-28.7 °C with an average of 27 (\pm 1) °C. The Brahmani River has the higher water temperature (~1 °C) compared to that of the Mahanadi River. The conductivity of these river waters ranged between 42-170 µS with a mean value of 90 \pm 30 μ S; whereas, the mean conductivity for rainwaters is 6.4 μ S, very low compared to the river waters. The precipitation pattern of the peninsular Indian River basins is shown in Fig. 3.3 for the monsoon period of the years 2013 and 2014 (http://disc2.nascom.nasa.gov/ Giovanni/tovas/TRMMV6.3B43.shtml).



Fig. 3.2: The monthly river water and sediment discharge of the Godavari and the Mahanadi River Systems (Bikshamaiah and Subramanian, 1980; Chakrapani and Subramanian, 1990; http://www.grdc.sr.unh.edu).

Table 3.1: Major ions, TDS, NICB, CSI, Sr concentration and Sr isotopic composition from the Godavari, Mahanadi and the Brahmani River waters and dissolved Nd isotopic compositions in the GRS.

Sample ID	Na^+	\mathbf{K}^{+}	Ca ²⁺	Mg^{2+}	Cl	SO ₄ ²⁻	NO ₃	HCO ₃	SiO ₂	TDS	NICB, %	Sr	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	8 _{Nd}	CSI
Godavari Rive	er water															
GDV-13-01	216	48	226	46	126	47	17	601	173	74	-3.5	0.22	0.710013	0.512188	-8.8	-1.74
GDV-13-03	700	48	574	398	429	215	34	1582	280	202	8.8	1.35	0.709686	0.512263	-7.3	-0.82
GDV-13-04	2051	86	510	635	1432	479	0	2350	133	335	-6.6	2.17	0.709440	0.512306	-6.5	-0.85
GDV-13-06	1431	102	1147	733	1069	319	184	3181	314	394	4.3	3.77	0.709276	0.512325	-6.1	-0.58
GDV-13-07	1312	91	660	726	702	250	145	2916	337	334	-2.1	3.39	0.710749	0.512282	-6.9	-0.66
GDV-13-10	911	85	777	464	388	161	76	2437	211	262	7.9	2.37	0.711301	0.511828	-15.8	-0.61
GDV-13-12	1433	79	544	729	572	166	21	3621	282	351	-10.7	3.73	0.717729	0.511476	-22.7	-0.21
GDV-13-14	776	61	741	443	317	124	78	2688	307	271	-3.8	2.22	0.714780	0.511733	-17.7	-0.35
GDV-13-16	509	50	653	318	215	76	80	2321	324	228	-9.7	1.36	0.714213	0.511207	-27.9	-0.28
GDV-13-17	484	51	630	323	208	76	66	2099	297	211	-3.3	1.26	0.714402	0.511310	-25.9	-0.26
GDV-14/01	1548	89	790	595	748	311	27	2916	263	337	2.1	3.74	0.715746	0.511682	-18.6	-0.13
GDV-14/02B	409	46	494	252	150	69	56	1632	294	170	-1.5	1.13	0.714866	0.511418	-23.8	-0.61
GDV-14/05	392	47	465	228	156	73	59	1550	253	161	-4.6	1.10	0.714882	0.511632	-19.6	-0.81
GDV-14/02A	373	48	476	227	147	67	48	1526	245	158	-1.5	1.06	0.714499	0.511451	-23.2	-0.36
Tributaries of	Godava	nri														
GDV-13-02	535	46	415	303	248	95	17	1400	191	154	8.7	0.86	0.708871	0.512252	-7.5	-0.91
GDV-13-05	1828	118	1398	990	1334	405	606	4055	443	524	-1.2	4.88	0.709243	0.512372	-5.2	-0.26
GDV-13-08	1926	97	515	897	1385	307	108	2678	407	363	1.3	3.44	0.711017	0.512122	-10.1	-0.66
GDV-13-09	1396	74	848	508	570	164	71	3326	205	337	-2.6	3.45	0.720515	0.511228	-27.5	-0.15
GDV-13-11	731	52	580	596	229	69	83	2534	468	259	5.1	2.01	0.716805	0.511445	-23.3	-0.35
GDV-13-13	536	53	786	418	180	87	98	2509	368	252	1.2	1.57	0.712525	0.511755	-17.2	-0.20
GDV-14/03	208	30	224	143	73	22	35	878	303	97	-5.8	0.47	0.723004	0.511253	-27.0	-1.12
GDV-14/04	190	27	177	92	71	20	25	712	246	79	-10.9	0.37	0.737089	0.510955	-32.8	-1.35
GDV-13-15	300	35	264	137	176	24	31	896	226	101	-1.1	0.84	0.718242	0.511185	-28.3	-0.43

Sample ID	Na ⁺	\mathbf{K}^+	Ca ²⁺	Mg^{2+}	Cl	NO ₃	SO4 ²⁻	HCO ₃ -	Si	TDS	NICB, %	[Sr]	⁸⁷ Sr/ ⁸⁶ Sr	CSI
Mahanadi Ri	ver wat	ter												
MND-14/01	132	31	299	63	64	32	27	836	138	84.7	-10.2	0.540	0.716826	-1.71
MND-14/03	179	54	405	97	119	79	48	1041	84	108.2	-7.4	0.694	0.716372	-1.42
MND-14/05	222	30	353	103	70	47	34	1055	146	105.8	-6.2	0.732	0.719435	-1.46
MND-14/07	271	52	350	131	109	46	95	1036	169	115.7	-6.9	0.760	0.721648	-1.68
MND-14/09	259	31	475	158	102	51	44	1375	141	134.7	-3.7	0.889	0.719848	-0.62
MND-14/11	218	52	254	78	95	38	37	800	109	84.5	-7.2	0.653	0.718229	-1.81
MND-14/13	269	32	359	125	88	33	28	1185	143	114.8	-6.8	0.826	0.720485	-1.60
MND-14/15	93	35	144	62	25	ND	9	551	131	54.6	-9.2	0.314	0.728543	-2.22
Tributaries of	f Maha	nadi												
MND-14/02	318	60	653	179	162	86	74	1699	116	170.6	-2.6	1.118	0.715675	-1.00
MND-14/04	209	29	445	127	67	65	28	1266	100	120.5	-5.0	0.967	0.716255	-1.38
MND-14/06	253	40	492	162	97	56	77	1376	146	139.5	-5.0	0.908	0.721281	-2.02
MND-14/08	360	42	740	227	126	56	468	1180	153	180.3	1.6	3.294	0.712684	-0.61
MND-14/10	148	29	178	93	62	7	30	664	109	67.2	-9.6	0.357	0.727936	-1.83
MND-14/12	306	30	396	145	90	33	32	1278	147	123.9	-3.2	0.944	0.719159	-2.23
MND-14/14	218	29	295	97	73	27	20	961	119	93.2	-6.4	0.657	0.721351	-1.68
Brahmani Ri	ver wat	ter												
BMN-14 /04	188	47	224	111	77	27	60	736	158	83.1	-5.6	0.387	0.733260	-1.97
BMN-14/01	182	31	146	101	61	35	39	597	223	72.1	-8.2	0.338	0.731144	-2.24
Tributaries of	f Brahı	nani												
BMN-14/02	264	89	268	147	119	37	51	949	229	107.8	-2.0	0.498	0.725901	-1.50
BMN-14/03	189	49	231	117	80	26	68	757	147	85.1	-6.6	0.394	0.735955	-1.74
Rain water sa	mples													
RW - 01	33.7	5.2	12.1	4.3	33.2	9.2	10.8	15.8	0.6	5.4	-10.2	0.003	0.713497	-5.76
RW - 02	35.5	10.6	15.3	4.4	31.7	14.7	12.2	22.7	1	6.6	-8.4	0.010	0.713366	-4.92
RW - 03	38.5	6.6	14.4	4.1	38	9.7	11.2	18.9	0.8	6.1	-8.1	0.011	0.714092	-6.27

here, the units of Major ions = μ M; TDS = mg L⁻¹; and Sr = μ mol kg⁻¹.

In the present study, the major ion composition shows a good balance between total cations (TZ⁺) and anions (TZ⁻). The normalized inorganic charge balance (NICB; [(TZ⁺ - TZ⁻)/TZ⁻]) for the peninsular Indian River samples varies from 1.0 to 10.9%, which is well within the precision of measurements (Table 3.1). The NICB provides evidence that there is no significant contribution from organic acid and ligands to the charge balance. The dissolved silica (Si) in the GRS ranges from 173 to 468 μ M with an average of 286 ± 83 μ M; whereas, it varies from 84-230 μ M with an average value of ~140 ± 35 μ M in the Mahanadi and Brahmani River waters. Rainwaters are having Si, with a mean of 0.8 μ M, the order of magnitude lower compared to that in river waters.

Using pH, temperature and major ion composition of river waters, CSI was calculated for all the samples from the peninsular Indian River. In these river waters, CSI varies between -2.24 and -0.13. The CSI of all the samples is less than zero, indicating under saturation of these waters with respect to calcite.

The silicate fractions of the sediments from the GRS have been analyzed for major elements abundances, Sr-Nd concentrations and their isotopic compositions (Table 3.3). Fe and Al are the most abundant in the Godavari River sediments, followed by Ca, Mg, Ti, K, Na, and Mn. The Sr and Nd concentration of these sediments ranged between 40-385 μ g g⁻¹ and 5-25 μ g g⁻¹, respectively, and their respective isotope compositions vary with a wide range of 0.710841-0.949058 and -4.0 to -35.7 (Table 3.3).

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	(La/Yb) _N	Ce*
							pmol kg	g-1								
Godavari Rive	er Main s	tream														
GDV-13/01	90.43	104.05	30.3	155.46	40.45	14.11	59.22	6.33	42.98	7.68	23.96	3.7	22.2	3.20	0.30	0.42
GDV-13/03	16.99	20.36	5.16	32.92	10.28	4.08	14.18	1.51	13.75	2.3	11.73	1.56	10.69	1.22	0.12	0.41
GDV-13/04	31.62	34.21	9.29	48.9	14.46	5.66	25.67	2.49	19.13	3.44	14.8	1.75	11.07	0.82	0.21	0.42
GDV-13/06	35.36	48.4	9.89	51.65	13.12	6.55	20.32	2.1	18.88	3.59	14.58	2.13	13.23	1.70	0.20	0.54
GDV-13/07	54.01	56.54	15.28	90.04	26.43	12.9	47.13	8.61	44.9	11.14	30.37	4.09	22.78	4.27	0.18	0.39
GDV-13/10	29.34	38.23	5.65	37.96	12.48	4.65	17.58	3.48	15.67	5.39	13.05	0.98	9.92	1.96	0.22	0.54
GDV-13/12	31.43	32.93	3.8	25.87	7.24	2.42	9.45	1.62	7.11	2.2	6.37	0.37	8.94	1.29	0.26	0.52
GDV-13/14	56.89	68.56	9.99	55.23	16.66	5.82	26.17	4.82	19.61	6.1	15.43	1.38	13.17	2.33	0.32	0.56
GDV-13/16	175.12	120.83	30.99	139.25	25.95	7.52	36.01	5.49	30.84	7.22	20.21	2.12	19.28	2.47	0.67	0.34
GDV-13/17	102.63	56.82	21.15	94.37	19.19	6	26.69	3.71	22.39	5.22	15.24	1.35	13.3	1.74	0.57	0.26
GDV-14/01	29.82	40.42	5.91	30.68	6.02	1.87	9.44	1.62	7.33	2.13	7.21	0.5	7.34	1.41	0.30	0.62
GDV-14/02A	105.47	76.18	23.9	102.94	21.89	6.7	28.88	4.25	22.17	4.27	15.77	1.78	12.4	1.62	0.63	0.34
GDV-14/02B	139.54	104.07	28.75	125.45	27.58	7.16	35.94	4.45	26.37	5.65	16.5	1.74	15.84	1.86	0.65	0.36
GDV-14/05	143.65	116.41	30.59	130.91	27.51	7.39	37.91	4.43	27.01	5.99	18.34	1.68	13.24	2.01	0.80	0.39
Tributaries																
GDV-13/02	23.96	39.58	6.86	39.34	9.69	3.96	17.87	1.59	14.04	2.48	9.7	1.47	7.83	0.3	0.23	0.62
GDV-13/05	29.6	56.35	10.42	59.73	18.28	7.97	33.03	4.15	35.78	7.16	27.24	3.17	20.26	2.33	0.11	0.64
GDV-13/08	22.03	25.24	3.97	18.85	5.53	2.54	7.91	1.41	7.1	2.04	6.77	0.57	6.94	1.83	0.23	0.56
GDV-13/09	92.32	63.65	18.9	86.41	16.91	4.69	25.03	4.03	24.64	6.73	19.8	2.28	15.2	2.26	0.45	0.32
GDV-13/11	58.8	44.93	9.93	43.72	9.81	2.93	13.63	3.09	8.25	3.58	6.16	0.37	5.38	0.74	0.81	0.39
GDV-13/13	69.08	44.63	15.93	72.42	17.33	5.76	29.82	3.87	26.09	6.49	19.11	2	15.95	2.16	0.32	0.29
GDV-14/03	179.49	171.19	41.08	177.5	31.32	9.16	44.46	5.02	30.48	7.27	17.41	1.85	14.16	1.85	0.94	0.44
GDV-14/04	366.38	409.91	93.56	366.29	60.58	13.81	75.33	10.72	46.3	10.33	24.95	2.75	18.26	3.27	1.48	0.52
GDV-13/15	394.7	378.37	81.96	293.91	57.74	13.33	59.35	8.42	40.24	7.82	21.94	2.27	17.69	2.51	1.65	0.49

Table 3.2: Concentration of dissolved REE of the Godavari, and the Mahanadi Rivers

Sample ID	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	(La/Yb) _N	Ce*
_							pmol k	g ⁻¹							-	
						Mal	nanadi H	River	water							
MND_14/01	389.4	400.6	88.7	332.0	61.8	14.3	81.28	8.1	43.6	7.6	24.8	2.86	19.9	2.72	1.44	0.50
MND_14/03	128.3	101.9	38.2	171.1	40.0	12.1	59.99	5.4	35.3	5.4	19.5	1.51	13.0	1.43	0.73	0.33
MND_14/05	394.2	325.9	79.4	287.0	47.1	11.6	57.71	5.8	33.7	5.0	19.5	1.40	13.7	1.78	2.13	0.42
MND_14/07	109.0	96.9	26.6	107.5	23.0	5.8	33.83	3.1	23.6	3.0	15.5	1.27	14.6	1.59	0.55	0.41
MND_14/09	54.3	33.0	14.0	65.0	13.4	3.8	17.64	1.9	15.0	2.3	10.4	1.12	10.6	1.35	0.38	0.26
MND_14/11	366.6	531.7	89.7	369.8	70.6	20.5	92.01	9.3	54.4	10.4	31.2	3.52	25.7	3.71	1.05	0.67
MND_14/13	300.4	285.5	72.7	286.2	54.7	15.4	81.09	8.3	53.2	9.8	32.5	3.81	25.5	3.39	0.87	0.45
MND_14/15	106.0	102.3	30.1	133.6	30.2	8.77	44.31	5.1	26.8	7.0	32.9	5.38	38.7	5.70	0.20	0.41
							Tribu	taries								
MND_14/02	128.2	111.3	33.6	145.4	32.8	9.8	45.99	4.7	28.2	5.2	16.7	1.71	13.0	1.65	0.73	0.38
MND_14/04	146.1	100.4	31.3	131.4	25.0	6.2	36.47	3.3	21.8	3.6	14.4	1.25	10.5	1.29	1.03	0.33
MND_14/06	148.9	144.7	34.5	142.9	32.1	8.9	47.31	4.6	31.6	5.8	20.2	1.64	16.2	2.01	0.68	0.45
MND_14/08	54.7	38.2	14.8	69.1	17.3	4.4	25.78	2.2	18.1	3.0	13.9	1.24	13.2	1.79	0.31	0.29
MND_14/10	198.3	201.2	47.4	193.1	36.1	9.9	51.43	5.5	31.9	5.5	19.4	2.07	16.7	2.44	0.88	0.47
MND_14/12	235.3	291.1	61.5	253.7	48.3	12.6	71.05	6.8	38.4	7.2	25.3	2.60	19.1	2.53	0.91	0.55
MND_14/14	196.5	169.5	47.4	201.4	40.2	13.2	75.79	9.0	64.1	13.6	42.2	5.20	35.4	5.45	0.41	0.39

Table 3.3: The Major elements, CIA, Sr-Nd concentrations and their isotopic compositions in the particulates

 of the GRS

Sample ID	Location	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	MnO	TiO ₂	CIA	Sr	Nd	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	٤ _{Nd}
					W	t %				%	μg	g ⁻¹			
River bank	Sediments														
GDV-13/05	Purna	1.02	0.53	4.78	3.16	11.79	24.54	0.29	1.96	49	130	13	0.710841	0.512433	-8.91
GDV-13/06	Godavari	1.53	0.64	7.83	4.00	10.03	13.83	0.20	2.90	64	219	10	0.708634	0.512178	-3.99
GDV-13/07	Godavari	1.12	0.65	3.66	2.18	7.77	12.03	0.11	4.28	57	179	12	0.711227	0.512095	-10.60
GDV-13/08	Manjira	0.96	1.01	2.91	2.49	9.72	11.94	0.14	5.42	65	160	13	0.725109	0.511874	-14.90
GDV-13/09	Peddavagu	1.34	3.80	0.79	0.67	5.81	1.15	0.03	0.12	45	151	5	0.784710	0.510716	-37.49
GDV-13/12	Godavari	1.35	1.87	2.46	2.32	10.15	9.54	0.05	1.88	61	214	21	0.727961	0.511104	-29.92
GDV-13/13	Pranahita	1.08	1.30	2.76	2.37	10.84	10.71	0.10	2.71	66	134	18	0.723579	0.511760	-17.13
GDV-13/14	Godavari	1.03	2.12	1.90	2.05	10.78	8.22	0.05	2.34	65	159	19	0.735215	0.511340	-25.31
GDV-13/15	Sabari	1.00	1.86	1.53	1.83	13.38	10.02	0.04	1.61	73	81	24	0.74988	0.511128	-29.46
GDV-13/16	Godavari	1.17	1.71	2.56	2.06	11.52	10.69	0.05	2.03	65	139	17	0.736214	0.511446	-23.25
GDV-14/02	Godavari	0.82	1.67	3.41	1.55	14.67	9.92	0.13	2.18	71	130	25	0.736363	0.511513	-21.94
GDV-14/04	Indravati	0.95	2.51	0.94		10.65	2.56	0.04	0.22	71	141	24	0.799137	0.510982	-32.30
River bed Se	ediments														
GDV-13/09	Peddavagu	1.70	4.18	1.03	0.39	9.38	1.02	0.02	0.06	53	203	5	0.778093	0.510809	-35.68
GDV-13/12	Godavari	2.45	1.53	4.62	3.02	10.65	9.36	0.07	0.53	52	384	25	0.715705	0.511009	-31.79
GDV-13/13	Pranahita	0.67	1.89	1.18	0.94	5.70	2.67	0.02	0.31	57	98	6	0.747922	0.511523	-21.75
GDV-13/15	Sabari	1.16	2.13	1.82	1.74	11.86	7.80	0.03	1.50	67	123	24	0.751806	0.511028	-31.41
GDV-13/16	Godavari	1.07	1.60	2.47	2.34	12.21	12.14	0.05	1.84	68	158	24	0.755564	0.511444	-23.29
GDV-13/17	Godavari	1.02	2.53	1.47	0.98	6.87	2.29	0.00	0.40	54	133	6	0.755278	0.511229	-27.48
GDV-14/03	Indravati	1.33	3.58	1.27		13.46	5.26	0.05	1.05	69	45	18	0.883469	0.510921	-33.49
Suspended I	Particulate M	atter													
GDV-13/05	Purna										40	15	0.714111	0.512123	-10.05
GDV-13/13	Pranahita	0.87	1.40	1.81	3.02	14.66	14.05	0.06	1.80	76	82	24	0.730678	0.511814	-16.08
GDV-13/14	Godavari	0.84	1.39	2.01	3.20	15.83	13.10	0.04	1.64	77	78	24	0.733001	0.511712	-18.06
GDV-13/16	Godavari	0.93	1.24	2.24	3.16	4.74	13.52	0.05	1.86	49	87	24	0.728092	0.511795	-16.45
GDV-13/18	Godavari	0.86	1.22	1.87	2.65	13.59	12.64	0.04	1.81	75	75	22	0.731446	0.511744	-17.45



Fig. 3.3: The plots show the monsoon rainfall (cm) patterns over the peninsular river basins during (a) 2013 and (b) 2014. These plots indicate that marginally higher precipitation occurred in the Godavari River basin during monsoon 2013, compared to 2014. However, the lower Godavari River basin received moderately more precipitation compared to the upper basin during the monsoon of 2014 (http://disc2.nascom.nasa.gov/Giovanni/tovas/TRMM V6.3B43.shtml).

3.3 Discussions

3.3.1 Spatial and inter-annual variations in major ions, TDS

Major ion compositions in river waters explain the chemical weathering in the basin which is the only process by which acidity from the atmosphere can be neutralized over the long period of time scale (Sarin and Krishnaswami, 1984; Palmer and Edmond, 1992; Krishnaswami et al., 1992, 1999; Edmond and Huh, 1997; Galy and France-Lanord, 1999; Dessert et al., 2001; Dalai et al., 2002; Singh and France-Lanord, 2002; Bickle et al., 2003, 2005; Das et al., 2005; Singh et al., 2005, 2006; Rai and Singh, 2007; Rengarajan et al., 2009; Rai et al., 2010).



Fig. 3.4: The plots show the TDS pattern in (a) the Godavari, and (b) the Mahanadi and the Brahmani Rivers and their tributaries. X-axis represents the location of sampling from heads waters to downstream.

The TDS in the river waters of the GRS varies within a wide range of 74-524 mg L⁻¹ with an average of 246 ± 115 mg L⁻¹ (n=23; Table 3.1). The TDS of the GRS shows spatial and temporal variations. In general, head waters of the Godavari River mainstream starts with low TDS, reaches to the maximum in middle reaches of the river and decreases downstream (Table 3.1; Fig. 3.4a). In the present study, the upstream tributaries of the GRS flowing through the Deccan Trap basalts are having high TDS (Fig. 3.4a). The Purna tributary, which is one of the major tributaries of the GRS in the upper reaches, delivers water with maximum TDS of 524 mg L⁻¹. The Indravati and the Sabari tributaries of the Godavari River erode gneisses in lower reaches of the GRS with low TDS, ~100 mg L^{-1} . In the middle reaches of the Godavari River, near Lakshettipet (GDV-13/12), TDS is 350 mg L⁻¹. TDS of the Godavari mainstream decreases (Table 3.1; Fig. 3.4a) after its confluence with the tributaries Pranahita, Indravati and the Sabari due to their lower TDS with the high water discharge. The low TDS in the Pranahita, Indravati, and the Sabari tributaries could be due to the higher rainfall and presence of relatively more weathering resistant lithology such as gneisses in their basins. The Pranahita flows through both the Deccan Trap basalts and gneissic rocks. Thus, in the upper basin of GRS, there is a high chemical weathering of the Deccan Trap basalts, whereas, low chemical weathering of gneisses is in the lower basin and moderate chemical weathering in middle reaches of GRS. The TDS of the GRS in the present study are slightly higher compared to the earlier reported data of Biksham and Subramanian, (1988b) and Jha et al., (2009) during monsoon (Fig. 3.5). The variations in TDS of the GRS can result from inter-annual differences either in runoff of the basin and/or change in land-use pattern.

The lower reaches of the Godavari have sampled again during monsoon, 2014 to investigate inter-annual variability in chemical composition and TDS (Fig. 3.5). Near Kaleswaram the TDS of the Godavari River, 337 mg L⁻¹ during monsoon, 2014 is higher compared to that observed in monsoon, 2013 (271 mg L⁻¹; Fig. 3.4a). However, the TDS in the Godavari mainstream near Bhadrachalam and Rajahmundry stations in the year 2014 are 170 and 160 mg L⁻¹, respectively,

which are significantly lower compared to those (228 and 211 mg L^{-1} respectively) at the same location during 2013 (Fig. 3.4a). These variations in TDS in the consecutive years are possibly due to variations in the rainfall in the basin during the monsoon, 2013 and 2014 (Fig. 3.3a, b). In the year of 2014, the Indravati basin received more precipitation compared to the other Godavari River basin (Fig. 3.3b). It concludes that during 2014 the Indravati discharged more water with less TDS (Table 3.1; Fig. 3.3b and 3.4a) resulting in dilution of the Godavari River waters delivered from the upstream of the GRS. On a global scale, in general TDS in the Godavari River waters is higher than those in the Amazon, the Yenissei, Congo, Lena and the Brahmaputra (Gaillardet et al., 1999). This may be due to higher weatherability of the basalts present in its basin.



Fig. 3.5: The plot shows the intra-annual variations of TDS in the Godavari River at Rajahmundry. The data compiled from Biksham and Subramanian, 1988b; Jha et al., 2009 and the present study. PM: Post-monsoon, Pr-M: Pre-monsoon, M: monsoon.

The dissolved chemical composition of the Mahanadi and the Brahmani Rivers along with a few of rainwater samples are listed in Table 3.1. The TDS values of the Mahanadi and the Brahmani River varies from 55 to 180 mg L⁻¹ with a mean of 108 ± 33 mg L⁻¹ (n = 19; Table 3.1) and are moderately lower compared to the earlier reported TDS values for the Mahanadi River (Chakrapani and Subramanian, 1990). In general, waters in the upper reaches of the Mahanadi River are high in TDS compared to its lower reaches (Table 3.1; Fig. 3.4b). The Seonath and Mand are tributaries of the Mahanadi River in the upper reaches delivering high TDS to the mainstream, and contributing significantly to the dissolved chemical composition of the Mahanadi River. As discussed earlier, these variabilities in TDS could arise due to rainfall variability in their sub-basins. Upstream basin of the Mahanadi receives lower rainfall compared to lower reaches (Fig. 3.3b). The similar variability of precipitation observed in the Brahmani River basin also leads to high TDS upstream and low TDS downstream. Thus, after lithology, precipitation acts as a controlling factor of the dissolved chemical composition of the Mahanadi and the Brahmani River systems.

The ternary plots of cations and anions in the Godavari, Mahanadi and the Brahmani River and rainwaters are shown in Fig. 3.6a, b. Na⁺ is the most abundant cation followed by Ca^{2+} in the GRS. The abundances of major cations in the GRS are in declining order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ (Table 3.1); whereas, alkalinity dominates in the anion budget followed by Cl⁻. These results indicate that the weathering of silicate and/or saline/alkaline soil is the dominant controlling factor of dissolved major ions in the GRS along with the carbonate weathering. However, Calcium (Ca^{2+}) is the most abundant in the cation budget of the Mahanadi and the Brahmani River waters followed by Na⁺. The declining order of major cations present in the Mahanadi and the Brahmani River waters is: $Ca^{2+} > Na^+ >> Mg^{2+} > K^+$ (Table 3.1). In the ternary plot of cations budget, most of the samples lie in between Ca^{2+} and $(Na^{+} + K^{+})$ apex and rainwaters are high in Na^+ compared to the other cations (Fig. 3.6a). Alkalinity (HCO₃⁻) is the dominant anion compared to Si and other anions of the Mahanadi and the Brahmani River waters. In rainwaters, $(Cl^2 + SO_4^{2-})$ are the most abundant compared to other anions (Fig. 3.6b). Chloride (Cl⁻) in these rivers is the second most abundant



Fig. 3.6: Ternary plots of (a) cations and (b) anions in the Godavari, Mahanadi and the Brahmani River and in rainwaters.

anion after alkalinity, may be because of the presence of halite and saline/alkaline soils and anthropogenic sources (Gaillardet et al., 1999) in their drainages. The decreasing order of abundance of anions in these rivers is: $HCO_3^- > Cl^- > SO_4^{2^-} > NO_3^-$. Alkalinity contributes on an average 75 (±10), 82 (±10) and 77 (±2) % of total anionic (TZ⁻) budget of the Godavari, Mahanadi and the Brahmani Rivers respectively.

 SO_4^{2-} is more abundant in the upper and middle stretch waters of the GRS compared to its downstream waters. The average SO_4^{2-} in the upper (GDV-13/01 to GDV-13/06), middle (GDV-13/07 to GDV-13/12) and lower stream waters (below GDV-13/12) are ~260, 220 and 85 μ M, respectively. The higher SO_4^{2-} in the upper and middle reaches of the GRS could be because of weathering of pyrites globules hosted in the Deccan basalts (Roy-Barman et al., 1998). However, SO_4^{2-} varies from moderate to very high in these rivers, 9 to 468 and 40 to 70 μ M with an average of about 70 and 50 μ M in the Mahanadi and the Brahmani Rivers respectively. The consistent SO_4^{2-} in these river waters could be derived from the pyrites, black shales and/or evaporites. δ^{34} S of dissolved SO_4^{2-} in Krishna River (Das et al., 2011), however, indicate basalt sulfides as a minor source of SO_4^{2-} in these waters.

In the anion ternary plot (Fig. 5b), the majority of data points fall along the HCO_3^- - (Cl⁺+SO₄²⁻) joins; indicating that weathering of carbonates, evaporites and sulfides are in leading role. The abundances of NO₃⁻ in the Godavari, Mahanadi and the Brahmani River waters are between 1-600, 7-86 and 25-35 μ M with an average of ~90, 45 and 30 μ M respectively. In general, the utility of fertilizers in agriculture controls the abundance of NO₃⁻ to the river waters (Berner and Berner, 1996). The majority of the samples of the GRS are having NO₃⁻ below 100 μ M. The Purna and the Manjira tributaries are having NO₃⁻ of ~600 and 110 μ M respectively. These tributaries after their confluence with the Godavari River reflects their NO₃⁻ signature throughout the GRS. This might be the reason that, in the Godavari mainstream, the stations GDV-13/06 and GDV-13/07 after confluences of the Purna and the Manjira tributaries are having the

high NO_3^- of ~180 and 150 μ M, respectively. It indicates that, utilization of fertilizers is in excess in the upper Godavari Basin. However, in the Mahanadi and the Brahmani River, NO_3^- is on an average of 45 ± 20 and 30 ± 6 μ M, respectively, indicating that the moderate utilization of fertilizers in these river basins. Higher NO_3^- in these rivers could also be contributed from the dissolution saline/alkaline soils present in the basin.

Good positive correlation (r = 0.96, n=19) between Ca⁺ + Mg⁺ and HCO₃⁻ + SO₄²⁻ indicate that Ca⁺, Mg⁺, SO₄²⁻ and HCO₃⁻ are having common sources. The Mand, one of the tributaries of the Mahanadi River contains very high alkalinity and SO₄²⁻ concentrations compared to the other major cations, indicating additional source such as saline/alkaline soils contributing significant alkalinity and SO₄²⁻ to this river.



Fig. 3.7: The scatter plot of the total cation vs. CSI of the Godavari, Mahanadi and the Brahmani River waters. All the waters of the Godavari, Mahanadi and the Brahmani Rivers are under-saturated for calcites.



Fig. 3.8: The plots show the variability of dissolved ⁸⁷Sr/⁸⁶Sr in the (a) Godavari, (b) Mahanadi and (c) the Brahmani River systems from source towards sea. Solid black squares and circles with white border show mainstream, open squares and circles with black border represent tributaries of these river systems. The squares and circles represent the respective sampling periods during monsoon, 2013 and 2014.

The river waters show a positive correlation between Ca^{2+} and Mg^{2+} suggesting their common sources. In the GRS, enrichment of Mg^{2+} compared to Ca^{2+} in few of the samples could be inferred due to saline/alkaline contribution or pollution sources. Fig. 3.7 shows the scatter plot of the sum of cations in the Godavari, the Mahanadi and the Brahmani River waters over CSI of the same waters. Estimated CSI in all the waters are less than zero indicating no calcite precipitation and therefore no Ca^{2+} removal from these river waters.

Dissolved Si concentrations of the GRS vary from 133 to 468 μ M (Table 3.1), and are within the range of previously reported values by Biksham and Subramanian, (1988b); Jha et al., (2009). The Si values in the Godavari River are higher compared to that in the Amazon, Changjiang and the Ganga-Brahmaputra Rivers (Gaillardet et al., 1999). However, dissolved Si abundances in the Mahanadi and the Brahmani River lies between 85 to 260 μ M, which is lower compared to the published values of the Mahanadi River (Chakrapani and Subramanian, 1990). In the present study, SiO₂ accounts for 2-20, 5-15 and 10-20% of TDS in the Godavari, Mahanadi and the Brahmani River systems respectively.

3.3.2 Spatial and inter-annual variation in Sr concentrations and ⁸⁷Sr/⁸⁶Sr ratios

Sr concentrations and its isotopic compositions in the dissolved phase of the Godavari, Mahanadi and the Brahmani Rivers and their tributaries are measured for the first time. A significant variation in Sr concentrations and its isotopic compositions has been observed in these river systems. The concentration of Sr and ⁸⁷Sr/⁸⁶Sr ratios in the Godavari mainstream vary from 0.22-3.77 μ M and 0.70928-0.71575 respectively (Table 3.1; Fig. 3.8a); whereas, these variations in tributaries of the GRS are between 0.47-4.88 μ M and 0.70887-0.72300, respectively (Table 3.1; Fig. 3.8a). The upstream waters of the Godavari main channel and its tributaries are highly concentrated in Sr with low radiogenic ⁸⁷Sr/⁸⁶Sr ratios. The uppermost sample (GDV-13/01) of the Godavari mainstream is having exceptionally very low Sr concentration with low isotopic ratio (Table 3.1). This is due to low intensity weathering of basalts in the headwater basin of the Godavari River. The headwaters of the Godavari mainstream and its tributaries (GDV-13/01 to GDV-13/6) drain the Deccan Trap basalts. The GRS waters also drain the saline/alkaline soils present in their drainage. These lithologies could be cause for high Sr abundances with low radiogenic ⁸⁷Sr/⁸⁶Sr ratios. The ⁸⁷Sr/⁸⁶Sr ratios in the middle reach (GDV-13/07 to GDV-13/12) of the GRS are moderate to high radiogenic. However, ⁸⁷Sr/⁸⁶Sr in the tributaries, the Manjira (GDV-13/08), Peddavagu (GDV-13/09) and the Kaddam (GDV-13/11) are quite radiogenic as they drain the Archean schists and gneisses of Dharwar craton (Fig. 3.1).

Even though the tributaries, the Peddavagu and the Kaddam are low in water discharge they contribute significantly high radiogenic ⁸⁷Sr/⁸⁶Sr to the GRS in the middle reaches of the Godavari mainstream (GDV-13/12; Fig. 3.1 and 3.8a). In the lower reaches of the GRS, the Pranahita (GDV-13/13) flows with huge water discharge through the Deccan Trap basalts, eastern granites, and saline/alkaline soils present in the basin with moderate Sr concentration (1.57 μ M) and ⁸⁷Sr/⁸⁶Sr ratio (0.71253). The Pranahita waters dilute Sr concentrations and its isotopic compositions of the Godavari mainstream at Kaleswaram (GDV-13/14) after its confluence. The major tributaries, the Indravati and the Sabari drain through eastern granite rocks and discharge huge amount of fresh water with low TDS and Sr concentrations with high radiogenic ⁸⁷Sr/⁸⁶Sr ratios (Fig. 3.8a). Due to their lower Sr concentrations with high water discharge, it dilutes waters of the Godavari mainstream. After mixing with all the tributaries, the Godavari River flows into BoB with Sr concentration of 1.18 (\pm 0.8) µmol kg⁻¹ and ⁸⁷Sr/⁸⁶Sr of 0.714642 (\pm 0.000150).

Downstream of the GRS near Kaleswaram, Bhadrachalam and Rajahmundry, water samples were collected in two consecutive monsoon seasons of 2013 and 2014 (Table 3.1) and analyzed for Sr concentration and its isotope composition. The results are listed in Table 3.1 (Fig. 3.8a). The measured ⁸⁷Sr/⁸⁶Sr ratios at Rajahmundry in the Godavari main stream in two consecutive

monsoonal years 2013 and 2014 are 0.71440 and 0.71488, respectively, which are lower compared to the published data near the location (0.7163; Trivedi et al., 1995). These inter-annual variations of Sr concentrations and its ⁸⁷Sr/⁸⁶Sr ratio could result from the observed variation in the precipitation (Fig. 3.3) in different sub-basins of the GRS during these two years. The high precipitation during monsoon, 2013 caused more weathering of the Deccan Trap basalts of less radiogenic ⁸⁷Sr/⁸⁶Sr ratios leading to lowering the ⁸⁷Sr/⁸⁶Sr of the Godavari River water at Rajahmundry. The higher precipitation during monsoon 2014 (Fig. 3.3) in the Indravati compared to the other sub-basins of the GRS resulted in more radiogenic ⁸⁷Sr/⁸⁶Sr compared to 2013. At its outflow, the Godavari River delivers ⁸⁷Sr/⁸⁶Sr of 0.714642 (\pm 0.000150) into BoB, marginally higher compared to the average global river ⁸⁷Sr/⁸⁶Sr ratio (0.712; Palmer and Edmond, 1992).

The dissolved Sr concentrations and its isotope ratios of the Mahanadi River basin vary from 0.31-3.29 μ mol kg⁻¹ and 0.712684 to 0.728543, respectively (Table 3.1; Fig. 3.8b). However, the Brahmani River basin has lower Sr concentrations with more radiogenic ⁸⁷Sr/⁸⁶Sr ratios. In the Brahmani River waters, Sr concentration and ⁸⁷Sr/⁸⁶Sr vary from 0.34 to 0.50 μ mol kg⁻¹ and from 0.725901 to 0.735955, respectively (Table 3.1; Fig. 3.8c). In the Mahanadi River basin, upstream waters have low ⁸⁷Sr/⁸⁶Sr ratios compared to the downstream waters (Fig. 3.8b). In the Brahmani River basin, the ⁸⁷Sr/⁸⁶Sr is more radiogenic in the Shank tributary compared to the Koel tributary (Fig. 3.8c).

3.3.3 Sources of Major ions and Sr in the peninsular Indian Rivers

Chemical weathering of various lithologies present in the basin, dissolution of evaporites, atmospheric and anthropogenic inputs could be the primary sources of the dissolved chemical composition in the river systems (Sarin and Krishnaswami, 1984; Krishnaswami et al., 1999; Gaillardet et al., 1999; Dessert et al., 2001; Dalai et al., 2002; Singh et al., 2006; Rengarajan et al., 2009; Rai et al., 2010). Atmospheric deposition in the form of precipitation (rain), which is derived from marine, terrestrial and anthropogenic inputs, could also be a considerable source of major ions to river waters (Krishnaswami et al., 1999; Dalai et al., 2002; Rai et al., 2010; Tripathy et al., 2010). The GRS drains through the Deccan basalts, eastern and western Dharwars, granites and saline/alkaline soils present in the basin. However, the Mahanadi and the Brahmani River erode the granites, gneisses, lower and upper Gondwana rocks, charnockites, khondalite suit and coastal sediment cover. By determining the abundances of major ions derived from various sources (e.g., silicates/carbonates, evaporites, atmospheric deposition etc.), silicate, carbonate weathering rates and CO₂ consumption rate (CCR) of the river basins can be assessed.

The Godavari River basin comprised of silicate minerals of the Deccan Trap basalts and gneissic rocks, and carbonates, whereas, the Mahanadi and the Brahmani River basins consist of silicate minerals of Gondwana, charnockites, khondalite suit, gneissic rocks and carbonates. The presence of Cl⁻ indicates atmospheric and evaporite sources and Cl⁻ corrected Na⁺ (Na^{*} = Na⁺_{riv}– Cl⁻_{riv}) in the river basins, in general, represent silicate-derived component. The calculated atmospheric contribution of Na⁺ in the Godavari, Mahanadi and the Brahmani Rivers is about 35-70, 25-65 and 35-45%, respectively. Na⁺ is also contributed by saline/alkaline soils whose dissolution contributes significantly to the Na⁺ budget (Drever and Smith, 1978; Rai et al., 2010). Five sources, (1) the Deccan Trap basalts, (2) gneissic rocks, (3) carbonates, (4) saline/alkaline soils and (5) precipitation can contribute to the major ion composition and TEIs of the Godavari River water chemistry. However, three sources namely (i) silicates from Gondwana, charnockites, khondalite suit and gneissic rocks, (ii) carbonates, and (iii) precipitation can contribute to the major ion composition and TEIs of the Mahanadi and Brahmani River water chemistry. Contributions from possible sources to the major ion budget and composition of Sr in river waters can be derived using forward model (Galy and France-Lanord, 1999; Krishnaswami et al., 1999; Dalai et al., 2002; Das et al., 2005; Singh et al., 2005; Tipper et al., 2006) using suitable proxies, such as Na_{sil} (= Na^+_{riv} - Cl^-_{riv}); $K^+_{sil} = K^+_{riv}$ etc. or inverse model (Negrel et al., 1993; Gaillardet et al., 1999; Millot et al., 2003; Wu et al., 2005; Moon et al., 2007; Tripathy and Singh, 2010, Rahaman and Singh, 2012; Goswami et al., 2014). The previous study by Jha et al., (2009) in the GRS

used the forward model to apportion the sources of dissolved cations. In the present study, I approached the inverse model (Tripathy and Singh, 2010) to assign the contribution of the cation budget and Sr composition from different sources present in the dissolved phase of the GRS, whereas, forward model to assign the contribution of the cation budget and Sr composition from a variety of sources present in the dissolved phase of the Mahanadi and the Brahmani River basins.

3.3.4 Inverse Modeling

Inverse modeling has been used to determine the contribution of the cation budget and Sr composition from a variety of sources to the river waters (Negrel et al., 1993; Gaillardet et al., 1999; Millot et al., 2003; Wu et al., 2005; Moon et al., 2007; Tripathy and Singh, 2010). The inverse model estimates not only the contribution of different sources to the dissolved chemical budget of the river but also the best-fit values for elemental ratios of the end-members (Negrel et al., 1993; Tripathy and Singh, 2010). In general, the inverse modeling calculations approached through a set of mass balance calculations (eq. 3.1-3.3) which describes the relation between observed data and model parameters.

where, E = Cl, Mg, Ca, HCO₃, Sr and (E/Na)_i is the molar ratio of element E to Na from the end member i. (E/Na)_{riv} is the molar ratio in rivers and f_i (Na) is the fraction of Na supplied from the ith end member. In the present study, (1) the Deccan Trap basalts, (2) gneissic rocks, (3) carbonates, (4) saline/alkaline soils and (5) the atmospheric deposition are considered as end members to the GRS waters. The above weighted fit calculations (eq. 3.1-3.3) were solved using the Quasi-Newton method (Tarantola, 2005).

To assign the contribution from several sources of dissolved chemical composition of rivers one can use inverse modeling by means of a single sample or over all samples of the basin at a time (Negrel et al., 1993; Moon et al., 2007). In the present study, all samples of GRS are modeled together to differentiate the number of mass balance equations which can provide the best fit for the *a posteriori* end member values for the basin. Silicate and carbonate contributions to the solute budget are calculated after obtaining the *a posteriori* model parameters for different sources.

3.3.4.1 a priori values of end-members

The *a priori* values listed in Table 3.4, which are considered using the possible data of multiple sources. Since Na behaves conservative in riverwater with minimum sources and it does not suffer removal like Ca (calcite) and Si, Mg (biological activities) in river waters, the *a priori* values in Table 3.4, were Na normalized elemental ratios (Tripathy and Singh, 2010). The Na normalized elemental and Sr isotope ratios for the atmospheric deposition (derived from marine, terrestrial and anthropogenic inputs) calculated from rainwater chemical composition reported for the Godavari River basin (Biksham and Subramanian, 1988b; Pillai et al., 2001; Salve et al., 2006, 2008). The elemental and isotopic compositions of carbonate end members were calculated using the reported conventional carbonate composition by Millot et al., (2003). However, the end members of the saline/alkaline soils are taken from Chatterjee (2013). The available abundances of elemental and isotopic compositions present in the Deccan Trap basalts are used to calculate their end-member ratios (Lightfoot and Hawkesworth., 1988; Peng et al., 1994; Chandrasekharam et al., 1999; Mahoney et al., 2000; Das et al., 2005 and 2006; Peng et al., 2014). The end members of the elemental and isotopic ratios for the gneissic rocks were calculated using the published data available in the lower and upper GRS (Jayananda et al., 2000,

2006 & 2013a, b; Dwivedi et al., 2011; Wani and Mondal, 2011; Nelson et al., 2014; De et al., 2015 and unpublished data from this study). Since the results of the inverse model are independent of $(E/Na)_i$ and $f_i(Na)$ the data were modeled even there is a significant uncertainties in Na normalized elemental ratios (Tripathy and Singh, 2010).

3.3.4.2 a posteriori values

The *a posteriori* values, the outcome of the inverse modeling end members of various sources to the GRS are listed in table 3.5. Using these Na normalized ratios, the cation compositions of all the sources are distinguished and then the silicate-derived cations were calculated in the GRS. The a posteriori values are low compared to *a priori* values except for carbonate end members, all the other end members are within the uncertainties of the calculation. Inverse model results show the contribution from rain, carbonates, saline/alkaline soils, the Deccan Trap basalts, and Archean gneisses range within 7-35%, 5-30%, 5-70%, 0-50% and 0-50%, respectively, to the Na⁺ budget in the GRS. The Deccan basalts do not contribute to the cation budget of the tributaries, the Indravati and the Sabari, as basalts are not exposed in these sub-basins. Similarly gneissic rocks of Dharwar do not contribute to cations in the upper reaches of the Godavari (GDV-13/01 to GDV-13/06). Using a posterior values, the contribution of cations from silicate minerals and carbonate rocks are determined and these cation budgets are used to calculate the chemical erosion rates of the GRS. Using cations derived from silicate minerals, the CO₂ consumption rate of the GRS are also estimated.

3.3.5 Forward Modeling in the Mahanadi and the Brahmani basins

Forward modeling is used to determine the cation budget and Sr concentration and its isotope composition from several sources to the river waters (Galy and France-Lanord, 1999; Krishnaswami et al., 1999; Dalai et al., 2002; Das et al., 2005; Singh et al., 2005; Tipper et al., 2006). The forward model relies on the use of Na corrected for atmospheric deposition and evaporites, (Na^{*} = Na_{riv}-Cl_{riv}) as an index of silicate weathering contribution along with the

Ratios	Rain	Carbonate	Sal/Alk	Deccan	Archean	Rain	Carbonate	Sal/Alk	Deccan	Archean
	#	\$	£	¥	§					
								Errors		
Cl/Na	1.33	0	0.14	0	0	1.13	0	0.17	0	0
Mg/Na	0.78	20	0.03	3.4	0.73	1.21	8	0.03	1.84	2.83
Ca/Na	2.08	50	0.01	2.63	0.46	3.06	20	0.03	1.42	1.39
Alk/Na	0.71	100	0.53	2	4	1.04	40	0.43	1	2
$Sr/Na \times 10^3$	3.4	75	0.13	4.93	2.43	3.14	25	0.24	2.01	4.1
⁸⁷ Sr/ ⁸⁶ Sr	0.70954	0.709	0.72089	0.70815	0.79677	0	0	0.01	0	0.08

Table 3.4: Na normalized element ratios, ⁸⁷Sr/⁸⁶Sr in rain, carbonates, saline/alkaline soils, Deccan and Archean end members

#: Biksham and Subramanian, 1988c; Pillai et al., 2001; Salve et al., 2006, 2008; \$: Conventional carbonate composition (Millot et al., 2003); £: Chatterjee, (2013) Ph.D. Thesis; ¥: Lightfoot and Hawkesworth, (1988); Peng et al., (1994 and 2014); Chandrasekharam et al., (1999); Mahoney et al., (2000); Das et al., (2005 and 2006); §: Jayananda, (2000, 2006 & 2013a, b); Dwivedi et al., (2011); Wani and Mondal, (2011); Nelson et al., (2014); De et al., (2015) and data from this study.

Table 3.5: *a posteriori* values of various end members contributing to the GRS, obtained from the inverse model

Ratio	Rain	Carbonate	Sal/Alk	Deccan	Archean	Rain	Carbonate	Sal/Alk	Deccan	Archean
								Errors		
Cl/Na	1.67	0	0.74	0	0	0.16	0	0.06	0	0
Mg/Na	0.04	1.28	0.01	1.05	0.46	0.05	0.13	0.01	0.09	0.07
Ca/Na	0.09	4.31	0.01	0.23	0.01	0.11	0.35	0.02	0.1	0.05
Alk/Na	0.15	12.06	0.43	1.5	1.79	0.22	0.97	0.15	0.36	0.31
$Sr/Na \times 10^3$	4	3.78	0.02	2.22	2.33	0.73	0.52	0.04	0.36	0.37
${}^{87}{ m Sr}/{}^{86}{ m Sr}$	0.70954	0.70898	0.72088	0.70809	0.74805	0	0	0.01	0	0.05

estimated values of Na normalized Ca and Mg based on their abundances in silicates present in the basin and are listed in Table 3.6. The silicate component of Ca and Mg (Ca_{sil}, Mg_{sil} in moles kg⁻¹) can be derived as:

$$\begin{split} Ca_{sil} &= Na_{sil} \times (Ca/Na)_{riv} & \dots & 3.4 \\ Mg_{sil} &= Na_{sil} \times (Mg/Na)_{riv} & \dots & 3.5 \\ K_{sil} &= K_{riv} & \dots & 3.6 \end{split}$$

The evaluated silicate derived cations $(\Sigma Cat)_{sil}$ defined as

here, the subscripts sil and riv represents silicate and river respectively. From these results, the fraction of cation contributions from the silicates to the rivers, $(\Sigma Cat)_{sil}$, can be determined as

The total cations budget derived from weathering of silicate minerals contributes about 20-40% with an average of 31 (\pm 6) % of the total riverine cations budget.

Table 3.6: Na normalized chemical composition of Eastern Indian Cratons, Eastern Ghats Mobile Belt (EGMB), carbonates and rain end members along with their errors from the Mahanadi and the Brahmani River basins.

Ratios	EIC #	±	EGMB @	±	Carbonates \$	±	Rain §	±
Cl/Na	0.00	0.001			0.00	0.00	0.960	0.054
Ca/Na	0.24	0.070	3.94	1.13	50.0	20.00	0.390	0.038
Mg/Na	0.08	0.050	4.18	1.13	20.0	8.00	0.120	0.012
Sr/Na	2.40	1.100	600	200	75.0	25.00	0.230	0.111
⁸⁷ Sr/ ⁸⁶ Sr	0.9085	0.250	0.7520	0.040	0.7090	0.0010	0.71365	0.00039
HCO ₃ /Na	0.50	0.200			100	40.00	0.530	0.093

EIC: Eastern Indian Cratons; EGMB: Eastern Granite mobile belt;

#: Sarkar and Saha, (1977); Sarkar et al., (1979, 1993); Iyengar et al., (1981); Vohra et al., (1991); Bhaskar Rao et al., (1992); Bhanumati and Ray, 2000; Chaki et al., (2008); Singh and Krishna, (2009); Dwived et al., (2011). @: Bhanumati and Ray, 2000 and references in it. \$: Conventional carbonate composition (Millot et al., 2003) and; \$: Present study data.

3.3.6 Chemical weathering rates

In the present study, using the respective water flux, drainage area and silica and major cation concentrations in silicate and carbonate components of modern river basins, chemical erosion rates such as, silicate and carbonate erosion rates (SER and CER) and CO_2 consumption rate (CCR) are determined.

3.3.6.1 Silicate erosion rate

The SER can be estimated using silica ($Si = H_4SiO_4$) and cation budget (Na_{sil} , K_{sil} , Ca_{sil} and Mg_{sil}) contributed through the silicate-weathered rocks/minerals. The SER calculated using the following equation

where, Q is the river water discharge, A is the river drainage area, $Z_{sil} = Na^+$, K^+ , Ca^{2+} and Mg^{2+} (mg L⁻¹) from silicate fraction calculated using inverse/forward modeling. The SER in the Godavari, Mahanadi and the Brahmani River basins, varies from 4.0-22.8, 4.9-11.3 and 6.5-10.4 tons km⁻² y⁻¹ respectively (Table 3.7). To understand the major controlling factor of SER in the Godavari, Mahanadi and the Brahmani River basins, we plotted the SER in these river basins over their runoff (Fig. 3.9). The headwaters of GRS draining basalts are having higher SER, whereas rivers like the Indravati, the Sabari in downstream of GRS draining gneissic rocks have lower SER. The SER in the middle reaches of GRS, which flow through both basalts and gneissic rocks are in between head and downstream waters. However, in the Mahanadi and the Brahmani Rivers the SER is lower for the same runoff. Fig. 3.9 clearly indicates that, lithology plays a primary role in determining SER followed by runoff of the river basin.

SER in the Godavari, Mahanadi and the Brahmani River basins along with the global major rivers are compared in Table 3.8. The silicate derived TDS is much higher in the GRS, compared to the world major rivers like Amazon and Congo (Table 3.8). The SER of the GRS also high compared to those global major rivers for the same runoff.



Fig. 3.9: The plot shows the SER vs. runoff in the Godavari, Mahanadi and the Brahmani River basins. The SER of the Godavari, the Mahanadi and the Brahmani, in general, correlates positively with runoff. The presence of two types of silicates, basalts and gneisses in their basins are responsible for the scatter in the plot. Rivers draining the Deccan Traps have higher slope whereas those draining gneissic lithology such as the Indravati, the Sabari, the Mahanadi, and the Brahmani are having lower slopes on the plot of SER vs. runoff due to their different weatherability as basalts weather faster compared to gneisses. Thus, runoff seems to be the dominant control on SER after the lithology of the basin.

3.3.6.2 Carbonate erosion rate

The carbonate erosion rate is calculated using the following equation

$$CER = \left(\frac{Q}{A}\right) \times \left[(100 \times Ca_{car}) + (84.3 \times Mg_{car}) \right] \qquad \dots 3.10$$

where, Ca_{car} and Mg_{car} are the respective molar abundances of Ca and Mg in carbonates. A wide spread of CER in the Godavari, Mahanadi and the Brahmani River basins exists from 3-50, 8.1-51.5 and 9.1-14.6 tons km⁻² y⁻¹, respectively (Table 3.7; Fig. 3.10), which is ~1-5 times of SER in their respective rivers. Fig. 3.10 shows the variations of CER with runoff of the river basins, indicating that runoff play primary role of CER in GRS. CER seem to be independent of runoff in some of the tributaries of the Godavari and in the Mahanadi and the Brahmani. CER in these sub-basins is limited by the carbonate exposures. The CER in the Godavari, Mahanadi and the Brahmani River basins along with the global major rivers are compared in Table 3.8.



Fig. 3.10: Plot shows the CER over runoff in the Godavari, Mahanadi and the Brahmani River basins indicating that runoff is the dominant factor controlling CER.

3.3.6.3 CO₂ consumption rate

Silicate weathering uptakes the atmospheric CO_2 and stabilizes the atmospheric temperature. In the present study, using major cation budget sourced from silicate minerals, CCR has been estimated from:

here, CCR expressed in units of mole km⁻² y⁻¹. The CCR in the Godavari, Mahanadi and the Brahmani River basins by silicate weathering varies with a wide range of $(1.2-9.0, 1-2, 0.8-1.4) \times 10^5$ mole km⁻² y⁻¹, (Table 3.7) respectively. The CCR in the head-water basin of the GRS with basalt lithology lies between ~2-4 × 10⁵ mole km⁻² y⁻¹, similar to those reported (~4 × 10⁵ mole km⁻² y⁻¹) for the Deccan basalts (Das et al., 2005; Jha et al., 2009). The CCR due to silicate weathering in the upper reaches of the GRS is ~2 times higher compared to that of the lower Godavari basin, indicating higher silicate cations released from the Deccan trap basalts. The CCR by the silicate erosion in these river basins is higher than the global average CCR (0.9×10^5 mole km⁻² y⁻¹; Gaillardet et al., 1999). The total CO₂consumption by silicate weathering in the Godavari, the Mahanadi and the Brahmani River basin is 5.23, 1.80 and 0.30 × 10¹⁰ mole y⁻¹ respectively, which account for ~0.60, 0.21 and 0.033% of the global CO₂ consumption (870 × 10¹⁰ mole y⁻¹; Gaillardet et al., 1999) due to silicate weathering.
Table 3.7: The SER, CER, Sr fluxes derived from silicate and carbonates weathering processes and CCR by silicate-weathering along with the river discharge, drainage area and basin runoff of the Godavari, Mahanadi and the Brahmani River basins

Sample ID	River/Location	Discharge	Area	Run off	ff Sr flux, Mmol y ⁻¹		SER	CER	CCR	
		10 ¹² L y ⁻¹	10^3 km ²	cm yr ⁻¹	Sil.	Carb.	tons l	$xm^{-2}y^{-1}$	10 ⁵ mole km ⁻² y ⁻¹	
Godavari mai	nstream									
GDV-13/01	Trimbak									
GDV-13/03	Newasa,	3.2	9.57	33	1.48	1.28	9.9	19	2.59	
GDV-13/04	Nath Sagr Res.	5.3	21.98	24	4.76	1.90	8.1	12	3.64	
GDV-13/06	Nanded	8.0	54.00	15	7.57	6.54	6.9	17	2.37	
GDV-13/07	Basar	11.0	87.00	13	15.67	5.43	7.2	9	2.68	
GDV-13/10	Sriramsagar Res.	20.0	90.00	22	20.26	11.62	7.5	18	2.58	
GDV-13/12	Lakshettipet	30.6	119.40	26	64.46	13.53	14.5	16	5.75	
GDV-13/14	Kaleswaram	67.4	228.48	29	59.62	41.39	10.6	26	2.89	
GDV-13/16	Bhadrachalam	100.0	270.14	37	43.59	56.13	10.7	30	1.95	
GDV-13/17	Rajahmundry	106.0	315.43	34	43.10	56.11	9.2	25	1.82	
GDV-14/01	Kaleswaram	67.4	228.48	29	115.62	38.64	14.5	24	5.49	
GDV-14/02A	Bhadrachalam	100.0	270.14	37	42.64	40.53	8.3	21	1.57	
GDV-14/02B	Bhadrachalam	100.0	270.14	37	36.46	38.85	9.8	21	1.81	
GDV-14/05	Rajahmundry	106.0	315.43	34	41.89	40.50	7.8	18	1.49	
Godavari trib	utaries									
GDV-13/02	Pravara, Newasa	2.0	6.54	30	0.76	0.64	6.8	14	1.96	
GDV-13/05	Purna, Purna	2.8	15.58	18	3.76	2.84	11.8	26	4.05	
GDV-13/08	Manjira, Kandakurthi	2.0	30.84	6	3.07	0.70	4.0	3	1.43	
GDV-13/09	Peddavagu, Gandlapet	0.9	1.67	54	1.49	0.59	22.8	50	8.99	
GDV-13/11	Kadem, Kaddam	0.2	2.63	8	0.22	0.10	4.4	6	1.22	
GDV-13/13	Pranahita, Arjungutta	36.8	109.08	34	19.64	24.10	11.7	32	2.44	
GDV-13/15	Sabari, Kunavaram	13.6	20.43	67	3.66	2.99	12.1	21	1.65	
GDV-14/03	Indravati,	32.9	41.66	79	6.43	7.39	16.9	25	1.43	

	Bhopalapatnam								
GDV-14/04	Indravati, Belnar	16.4	20.23	81	2.69	2.63	14.1	19	1.23
Mahanadi Ma	instream								
MND-14/01	Mahanadi	7.26	13.36	54	1.19	2.73	6.5	18.0	0.66
MND-14/03	Mahanadi	24.81	47.26	52	3.61	13.61	4.9	24.6	0.70
MND-14/05	Mahanadi	25.41	48.41	52	9.26	9.34	8.0	20.6	1.21
MND-14/07	Mahanadi	29.05	59.60	49	11.30	10.79	8.7	20.0	1.30
MND-14/09	Mahanadi	31.16	69.23	45	11.71	15.99	6.8	25.2	1.07
MND-14/11	Mahanadi	45.88	90.63	51	13.60	16.36	6.5	14.2	1.09
MND-14/13	Mahanadi	54.11	96.19	56	23.54	21.17	9.1	23.0	1.53
MND-14/15	Mahanadi	70.48	125.31	56	28.71		7.1	8.1	1.44
Mahanadi Tri	butaries								
MND-14/02	Shivnath	14.64	30.03	49	5.49	10.88	7.2	36.8	1.30
MND-14/04	Jonk	1.70	3.24	52	0.58	1.06	6.3	26.7	1.13
MND-14/06	Hasdeo	4.34	10.07	43	1.62	2.32	6.8	25.0	1.06
MND-14/08	Mand	3.25	5.42	60	1.82	8.87	11.3	51.5	2.10
MND-14/10	Ib	9.00	12.45	72	1.86	1.36	7.7	16.6	1.03
MND-14/12	Ong	3.26	5.26	62	1.69	1.39	10.8	28.0	1.95
MND-14/14	Tel	13.51	23.25	58	4.70	4.18	7.7	19.3	1.28
Brahmani Ma	instream								
BMN-14/04	Brahmani	8.12	18.84	43	2.18	0.96	6.5	12.2	0.84
BMN-14/01	Brahmani	10.35	21.23	49	3.60		10.4	9.1	1.37
Brahmani Tri	butaries								
BMN-14/02	Koel	4.82	11.69	41	1.39	1.00	8.1	14.6	0.79
BMN-14/03	Sankha	3.13	6.97	45	0.82	0.42	6.5	13.3	0.87

here, Sil. and Carb. refers Silicate and Carbonate.

Table 3.8: The comparison of rivers water discharge, drainage area, runoff, silicate and carbonate erosion rates along with their CO_2 consumption rates due to silicate weathering along with the Indian and Global major rivers.

River	Discharge	Area	Runoff	SER	CER	CCR
	$10^{12} L y^{-1}$	10^3 km ²	cm yr ⁻¹	tons kn	$n^{-2} y^{-1}$	10 ⁵ mol km ⁻² y ⁻¹
Godavari	105	315	34	8.5 ± 1.0	21 ± 4	1.66
Mahanadi	70.5	125	56	7.1	8.1	1.44
Brahmani	10.5	20	50	10.4	9.1	1.37
Krishna, Alamatti	17.3	36.3	46.3	14	-	0.5-7.6
G-B	1050	1630	310	12.7	27.6	3.42
Amazon	6590	6112	107.8	13.1	11.1	0.52
Congo-Zaire	1200	1808	32.4	8.6	3.4	1.11
Global average	20000	54000	3040	-	-	1.61

All data from the compilation of Gaillardet et al., 1999; Galy et al., 1999; Das et al., 2005; Singh et al., 2005, 2008; Chaturvedi, 2012 and this study.

3.3.7 ⁸⁷Sr/⁸⁶Sr as a proxy of silicate weathering in the peninsular rivers

Application of dissolved ⁸⁷Sr/⁸⁶Sr in the rivers as a proxy of silicate weathering is still debated (Palmer and Edmond, 1992; Singh et al., 1998; Galy et al., 1999; Krishnaswami and Singh, 1998; Bickle et al., 2001, 2003, 2005; Oliver et al., 2003) particularly due the presence of highly radiogenic Sr in the Ganga drainage in the Himalaya (Quade et al., 2003; Singh et al., 1998). However, ⁸⁷Sr/⁸⁶Sr ratios are used as a proxy of silicate weathering in many drainage systems such as the Ganga, the Yamuna, the Brahmaputra, the Krishna, the Chambal etc. (Galy et al., 1999; Dalai et al., 2003; Bickle et al., 2005; Das et al., 2005; Singh et al., 2006; Rengarajan et al., 2009). In the present study the variation of dissolved ⁸⁷Sr/⁸⁶Sr ratios in the Godavari, Mahanadi and the Brahmani Rivers are plotted with SiO₂/TDS, a proxy of silicate weathering (Fig. 3.11a, b; Singh et al., 2005). Three trends are evident in the GRS (Fig. 3.11a); in the Mahanadi and the Brahmani River, ⁸⁷Sr/⁸⁶Sr linearly increases with SiO₂/TDS, albeit with scatter. Mixing of Sr derived from three types of silicates; basalts with lower ⁸⁷Sr/⁸⁶Sr and eastern/western gneisses with moderate and higher ⁸⁷Sr/⁸⁶Sr respectively with carbonates results in three trends in the GRS, whereas in the

Mahanadi and the Brahmani, linear variation (Fig. 3.11b) is due to mixing of Sr coming from silicates with high ⁸⁷Sr/⁸⁶Sr with that from carbonates having lower ⁸⁷Sr/⁸⁶Sr. Fig. 3.11 indicates that Sr isotopic composition can be used as a proxy of silicate weathering in the river basins of the peninsular India.



Fig. 3.11: The correlation of 87 Sr/ 86 Sr with the proxy of silicate weathering, SiO₂/TDS in the river basin of (a) the Godavari and (b) the Mahanadi and the Brahmani. 87 Sr/ 86 Sr ratio enhances with increasing SiO₂/TDS. The correlation of 87 Sr/ 86 Sr ratio with SiO₂/TDS represents it can be used as a proxy of silicate weathering.

3.3.8 Sources of dissolved Sr in the peninsular Indian Rivers

To examine the possible sources contributing to the Sr abundance and its isotopic composition, mixing plot between ⁸⁷Sr/⁸⁶Sr ratio and Ca/Sr ratio is used (Fig. 3.12a and b). The possible end members, namely the Deccan Trap basalts, saline/alkaline soils, carbonates and eastern/western granites are also plotted for the GRS waters (Fig. 3.12a). This demonstrates the ⁸⁷Sr/⁸⁶Sr ratio in head waters are controlled by basalt weathering whereas downstream waters are controlled by gneissic rock weathering along with a significant contribution from saline/alkaline soils and carbonates dissolution.

The Mahanadi and the Brahmani River basins drain through East Indian cratons, East Indian Ghats belt (EIGB) meta-volcanics and also erodes carbonates present in their basin. The dissolved chemical composition from these rivers also contributed significantly from anthropogenic sources through precipitation. Based on these primarily, viz., sources East Indian cratons, East Indian Ghats belt (EIGB) meta-volcanics, carbonates and atmospheric deposition a binary mixing plot using ⁸⁷Sr/⁸⁶Sr over Ca/Sr molar ratios is shown in Fig. 3.12b. The end members have been examined using several published data (Table 3.4 to 3.6).

To further constrain the silicate vs. carbonate Sr in the Godavari River, dissolved 87 Sr/ 86 Sr is plotted with 87 Sr/ 86 Sr in the silicate phase of sediments sampled at the same location (Fig. 3.13). The plot shows that the dissolved 87 Sr/ 86 Sr is nearly independent of silicate 87 Sr/ 86 Sr; in majority of the samples, the dissolved 87 Sr/ 86 Sr is very less than that of the silicates. A closer look at the data, however, indicates a marginal increase in dissolved 87 Sr/ 86 Sr with increasing silicate 87 Sr/ 86 Sr (inset Fig. 3.13) with a positive correlation (R²=0.67). Sr isotope composition of the waters is determined by its contribution from silicates, carbonates, and saline/alkaline soils. Therefore, the low radiogenic Sr isotopic compositions in the dissolved phase of the GRS can be due either to the lower contribution from silicates or dilution of radiogenic Sr from silicates by less radiogenic Sr from carbonates and other lithologies. Since, the silicates of the upstream drainage basins are less radiogenic in 87 Sr/ 86 Sr (0.705, Das et al., 2006; present study), the dissolved 87 Sr/ 86 Sr ratios are higher than the silicate phase

 87 Sr/ 86 Sr ratios in the head waters of the GRS. The other lithologies like carbonates and saline/alkaline soils present in the basin might have higher 87 Sr/ 86 Sr compared to the basalts.



Fig. 3.12: ⁸⁷Sr/⁸⁶Sr plotted with Ca/Sr (molar) ratio of waters samples from (a) the Godavari and (b) the Mahanadi and the Brahmani River basins along with a few of rainwaters. The end members values plotted for basalts, eastern and western gneisses, saline/alkaline soils, and carbonate are taken from published data (Table 3.4 to 3.6).

The estimated contribution of elemental Sr in the dissolved phase in the GRS from silicates is about 6-56% with an average of $38 \pm 10\%$. In the Mahanadi and the Brahmani River waters, silicates account for an average of 50 ± 25 and $75 \pm 20\%$ of elemental Sr, respectively.

In the Godavari, near Kaleswaram (GDV-13/14), there is almost no change in Sr flux from carbonates in the two consecutive years; however, the flux of silicate Sr during 2014 is double compared to 2013. However, near Bhadrachalam (GDV-13/16) and Rajahmundry (GDV-13/17) Sr fluxes from both silicates and carbonates during both the years were comparable.



Fig. 3.13: The scatter plot of dissolved ⁸⁷Sr/⁸⁶Sr in the GRS waters vs. ⁸⁷Sr/⁸⁶Sr of silicate phase of bed/bank and suspended sediments from the same location. The inset shows the same data plotted with expanded scale of the y-axis. It is seen from the inset that though ⁸⁷Sr/⁸⁶Sr of the Godavari waters vary with ⁸⁷Sr/⁸⁶Sr of silicate phase of sediment, the dissolved Sr are far less radiogenic than that of the silicate phase of sediments.

The total Sr fluxes from silicates and carbonates of the Godavari, Mahanadi and the Brahmani River basins have been determined using water discharge of the respective rivers and their Sr abundances determined from the inverse model. The chemical weathering in the Godavari, Mahanadi and the Brahmani Rivers deliver the dissolved Sr flux of 124, 22 and 3.6 Mmol y^{-1} to the BoB (Table 3.9) to their estuaries and hence to the Bay of Bengal.

Table 3.9: The fluxes of TDS, Sr and Nd in the dissolved and particulate phase of the Godavari, Mahanadi and the Brahmani River systems deliver into the Bay of Bengal.

River	TDS	diss. Sr	diss. Nd	part. Sr	part. Nd
	MT y ⁻¹	Mmol y ⁻¹	10 ³ mol y ⁻¹	M k	g y ⁻¹
Godavari	20	124	11.8	22.6	0.60
Mahanadi	4	22	9.4	n.a.	n.a.
Brahmani	0.75	3.6	n.a.	n.a.	n.a.

n.a.: Not available

3.3.9 Dissolved rare earth elements in the peninsular Indian rivers and ϵ_{Nd} behavior in the GRS

The concentration of REEs in the Godavari and the Mahanadi River waters and Neodymium isotopic compositions (ε_{Nd}) in the Godavari River waters were measured to construct their possible sources, fluxes and distribution patterns of dissolved REEs from these rivers to the BoB.

The abundances of the dissolved REEs along with the PAAS normalized La/Yb ratios, Ce anomaly (Ce*) of the Godavari and the Mahanadi River have been listed in Table 3.2. (La/Yb)_N expressed as.

$$\left(\frac{La}{Yb}\right)_{N} = \frac{\left(\frac{La}{Yb}\right)_{Sample}}{\left(\frac{La}{Yb}\right)_{PAAS}} \qquad \dots 3.12$$

whereas Ce anomaly (Ce*) expressed as,

where, the subscript N refers to PAAS normalized concentrations.

In the present study dissolved REEs of majority of the water samples are enriched in heavy REEs (HREEs) compared to lighter REEs (LREEs) with $(La/Yb)_N$ of ~0.50 (± 0.40) and 0.80 (± 0.50) in the Godavari and the Mahanadi Rivers respectively.

The respective PAAS normalized dissolved REE patterns of the Godavari and the Mahanadi River waters are plotted in Fig. 3.14a, b. PAAS normalized REE distribution patterns are similar in all the samples. In all the water samples, Ce displays negative anomaly (Table 3.2; Fig. 3.14a, b). The head waters of the GRS flowing through the Deccan basalts show PAAS normalized dissolved REE patterns enriched in HREEs with (La/Yb)_N varies between ~0.10 to 0.30. The Indravati and the Sabari tributaries draining Archean gneiss have (La/Yb)_N = 1.48 and 1.65, respectively, indicating that, LREEs are enriched than HREEs in these waters. The other tributaries and intermediate waters draining the Deccan basalts and/or gneisses have (La/Yb)_N of 0.30-0.94 with HREEs enriched REE pattern. In the present study, there is a wide variation existing in absolute abundances of the dissolved REEs. For example, concentration of La varies from ~16 to 400 pmol kg⁻¹and Yb lies between ~5 and 23 pmol kg⁻¹.

The PAAS normalized dissolved REE pattern show differences for various rivers and tributaries according to the lithology they drain (Fig. 3.14). The head waters of the GRS flowing through the Deccan Traps have very low LREEs than the HREEs. Whereas, the waters in downstream tributaries of the GRS namely the Indravati and the Sabari flows through gneisses have high LREEs than HREE. The intermediate waters contain both the basalts and gneissic chemical compositions.

The PAAS normalized dissolved REE patterns of the Mahanadi River waters have been plotted in Fig. 3.14b. In all the samples, PAAS normalized REEs distribution patterns are identical. Like the Godavari River waters the Mahanadi River waters also showing a negative anomaly in Ce (Table 3.2; Fig. 3.14b). The Mahanadi River waters drain silicate minerals of Gondwana, charnockites, khondalite suit, gneissic rocks and carbonates. In many of the samples, dissolved REE pattern shows enriched in HREEs with $(La/Yb)_N$ varying between ~0.20 to 2.10. Most of the main-streams waters in the Mahanadi River are enriched in LREE compared to their HREE, whereas, HREEs are enriched in tributaries. In the present study, there is a wide variation in absolute abundances of the dissolved REEs. For example, concentration of La varies from ~50-400 pmol kg⁻¹, whereas, concentration of Yb lies between ~10-40 pmol kg⁻¹.



Fig. 3.14: The distribution pattern of PAAS normalized REEs of the (a) Godavari and (b) the Mahanadi River waters.

The PAAS normalized dissolved REE patterns show coherent behavior in rivers according to the lithology they drain (Fig. 3.14b). In general, water are having enriched HREE pattern. The above discussion indicates that lithology is the major controller of the absolute abundance of dissolved REEs in the river waters.

3.3.10 Neodymium isotope composition in the GRS

The measured Neodymium isotope compositions (ε_{Nd}) in river waters of the GRS are listed in Table 3.1. The ε_{Nd} is distinct with spatial and inter-annual variations and vary from -5.2 to -32.8 (Table 3.1; Fig. 3.15) according to lithology they drain. The head waters of the GRS drain Deccan basalts, having high radiogenic ¹⁴³Nd/¹⁴⁴Nd ratios (ε_{Nd}). The upstream waters of the GRS, dissolved ε_{Nd} varies from -5.2 to -10.1. However, in the mid and lower tributaries of the GRS which flow through gneisses, are having ε_{Nd} values between -23.3 to -28.3. In the remaining mixed waters, ε_{Nd} values lies between -15.8 to -25.9 which are as a result of mixing of Nd derived from basalts and gneisses. In the present study, three sampling stations of the Godavari mainstream at Kaleswaram (GDV-13/14), Bhadrachalam (GDV-13/16) and Rajahmundry (GDV-13/17) have been sampled in monsoon season of two consecutive years, 2013 and 2014.



Fig. 3.15: The funnel diagram (not to scale) of the GRS shows the spatial and inter-annual variations of the dissolved Neodymium isotopic composition (ε_{Nd}) in the GRS. The black circles are city/town in the sampling way. The Godavari

River delivers 11.8×10^3 moles y⁻¹ of dissolved Nd to the BoB with a mean ϵ_{Nd} of -22.75.

The dissolved chemical composition of the Indravati River influences the chemical composition as well as the dissolved ε_{Nd} of the GRS significantly. Near Kaleswaram, ε_{Nd} in the consecutive years 2013 and 2014 were -17.7 and -18.6, respectively, indicating that the variation is the minimum or is within the measurement errors. However, in other locations near Bhadrachalam and Rajahmundry, the variation in ε_{Nd} is large, which are within about $\pm 5\varepsilon$ units (Table 3.1; Fig. 3.15). The variation in ε_{Nd} at these stations might be because of variation in weathering intensity of the different sub-basins.



Fig. 3.16: Dissolved ε_{Nd} in GRS vs. ε_{Nd} of silicate phase of bed/bank and suspended sediments from the same location. ε_{Nd} of the Godavari waters vary linearly with ε_{Nd} of silicate phase of sediment, the dissolved ε_{Nd} content is almost equal to ε_{Nd} in silicates of the GRS sediment.

Thus, after geology, runoff is the controlling factor on Neodymium isotopic compositions and the Indravati tributary contributes significant ε_{Nd} to the GRS. The ε_{Nd} of the Godavari (Fig. 3.15) suggests that near Bhadrachalam (after the confluence of the Godavari River with the Indravati tributary) the waters are not well mixed and dominated by the Indravati tributary waters, whereas at Rajahmundry these waters are well homogenized. Finally, the chemical weathering in the Godavari River, annually delivers 11.8×10^3 moles of dissolved Nd with -22.75 ± 3.35 ε_{Nd} to the BoB.

The scatter plot (Fig. 3.16) shows the relation between dissolved and silicate phase of bed/bank and suspended sediments ε_{Nd} from the same location. The dissolved ε_{Nd} shows a good positive correlation ($R^2 = 0.71$) with that of the silicates which follow almost 1:1 line (Fig. 3.16). It clearly indicates that the weathering of silicate minerals contributes to the ε_{Nd} in Godavari River waters without any fractionation. Fig. 3.16 indicates that dissolved Nd in the Godavari is derived from basalt with higher radiogenic Nd and from gneisses with less radiogenic Nd.



Fig. 3.17: The scatter plot shows the variation pattern of Al normalized Mn with Fe of sediments from the GRS.

3.3.11 The particulate chemical composition in the GRS

In the GRS, both bedload and suspended load sediments have been analyzed for major elements, concentration of Sr, Nd and their isotopic compositions to study their spatial and temporal variations in the GRS as well as the geochemistry of GRS. The measured major elements, Sr-Nd concentration and their isotopic compositions are listed in Table 3.3. Fe and Al are most abundant major elements in sediments of the GRS followed by Ca, Mg, Ti, K, Na and Mn. The ranges of Fe and Al abundances in the sediments of the GRS are, 0.8-17.16 and 2.5-4.38 wt%, respectively, which are within the typical range for rock forming minerals (Alagarsamy et al., 2010). The samples drain the Deccan basalts are more abundant in Fe compared to Fe. Even though Mn is lower abundant in sediments Mn/Al shows the linear trend with Fe/Al displaying the existence of Fe-Mn oxyhydroxides and the close association of Mn and Fe during weathering and erosion (Fig. 3.17).



Fig. 3.18: The plot shows the A-CN-K ternary distribution pattern of sediments from the GRS. The plot shows the Deccan is the dominant source of the sediments which undergone through variable chemical weathering evolving from the Deccan and mafic sources towards Al_2O_3 apex.

On A-CN-K (Al₂O₃-CaO + Na₂O-K₂O) ternary plot (Fig. 3.18) the majority of samples of the GRS are aligned close to Al₂O₃ and plot parallel to A-CN join indicating progressive chemical weathering of the samples originating from mafic compositions. The chemical index of alteration (CIA= $[Al_2O_3/(Na_2O + K_2O + CaO + Al_2O_3)] \times 100$; Nesbitt and Young, 1982) in the GRS, vary from 45 to 77, which is lower in the Deccan basalts region and higher in gneisses region (Table 3.3).

3.3.12 Provenance study using Sr and Nd Isotopic systematics

The concentration of Sr, Nd and their isotopic compositions are analyzed in the silicate fractions of the GRS sediments are listed in Table 3.3. The ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ε_{Nd} show significant spatial and temporal variations (Fig. 3.19). The ${}^{87}Sr/{}^{86}Sr$ and ε_{Nd} in the silicate fractions of the GRS sediments show wide variations of 0.710841 to 0.949058 and -4.0 to -37.5, respectively. The concentration of Sr, Nd in the GRS sediments varies from 40-400 μ g g⁻¹ and 5-25 μ g g⁻¹, respectively. Sediments from the upstream basin of the GRS occupied by the Deccan Trap basalts (Fig.3.1) have higher radiogenic ϵ_{Nd} and the less radiogenic $^{87}\text{Sr}/^{86}\text{Sr}.$ The mid and lower reaches tributaries of the GRS like the Peddavagu, Indravati and the Sabari erode chists and gneissic rocks with lower radiogenic ε_{Nd} and very high radiogenic ⁸⁷Sr/⁸⁶Sr. The tributaries, the Pravara, Kaddam and the Pranahita drain both the basalts and gneisses and deliver Nd and Sr with intermediate ε_{Nd} and ⁸⁷Sr/⁸⁶Sr ratios into the Godavari mainstream (Fig. 3.19). The results suggest that the Archean crusts contribute significantly to the sediment budget of the GRS. The ⁸⁷Sr/⁸⁶Sr ratios of the sediments near Bhadrachalam in two consecutive years 2013 and 2014 are 0.736214 and 0.736363 whereas; ε_{Nd} variations are -23.3 and -21.9, respectively (Fig. 3.19).

These inter-annual varieties in 87 Sr/ 86 Sr and ε_{Nd} might be because of variation in sources of the sediments due to variable runoff. The isotope compositions of the Godavari River sediments are primarily controlled by lithology of the basin they drain and followed by runoff of the basin. The GRS annually debouches about 170 MT of sediment load into the BoB which accounts

the flux of 22.6 M kg of Sr and 0.6 M kg of Nd (Table 3.9) with 87 Sr/ 86 Sr, 0.755278 and ε_{Nd} , -27.5. These 87 Sr/ 86 Sr and ε_{Nd} are higher compared to those reported for the outflow sediments of the Godavari (Ahmed et al., 2009).



Fig. 3.19: Funnel diagram (not to scale) of the Godavari mainstream and its tributaries showing variation in 87 Sr/ 86 Sr and ε_{Nd} for the monsoon, 2013 and 2014. The values in parenthesis are of suspended particulate matters (SPM).

⁸⁷Sr/⁸⁶Sr ratio and $ε_{Nd}$ of sediments from the various river and ocean basins have been used successfully to track their sources (Goldstein and O'Nions, 1981; Bouquillon et al., 1987; France-Lanord et al., 1993; Galy et al., 1996; Winter et al., 1997; Pierson-Wickmann et al., 2001; Clift et al., 2002; Singh and France-Lanord, 2002; Banner, 2004; Ahmad et al., 2005, 2009; Colin et al., 2006; Singh et al., 2008; Viers et al., 2008; Yang et al., 2008; Galy et al., 2010; Rahaman et al., 2011; Tripathy et al., 2011; Goswami et al., 2012; Awasthi et al., 2014; Ali et al., 2015; Damodararao et al., 2016). These isotope pairs are used as reliable proxies to track the sediment sources, as there are distinct differences in their composition in the different lithologies supplying these sediments. However, success to track the sediment sources reliably depends on their preservation during their weathering and transport. These processes may influence the isotope composition of Sr compared to that of Nd due to mobile nature of former making the Nd isotope composition more robust provenance tracer (Walter et al., 2000; Tutken et al., 2002). Robustness of Sr and Nd isotope compositions in tracking the sediment sources in the GRS could be verified by observing their relation with chemical index of alteration (CIA) and Al as they get influenced by the processes of size sorting and chemical weathering respectively which might affect the isotope composition of Sr and Nd of these sediments. ⁸⁷Sr/⁸⁶Sr and ε_{Nd} of the sediments of Andaman Shelf have been plotted with their CIA and Al content in Fig. 3.20 (a-d). These scatter plots do not show any interrelation among Sr-Nd isotope composition and Al content and CIA of the sediments suggesting the minimal influence of weathering and transport on these isotope composition and hence they can be used reliably to track the sources of these sediments.



Fig. 3.20: The scatter plots (a-d) show the distribution patterns of 87 Sr/ 86 Sr and ϵ_{Nd} with CIA and Al wt% in from the GRS. The absence of any correlation indicates preservation of source signature in them.

To estimate the principal sources of sediments present in the GRS, binary isotopes mixing curves have been plotted using their Sr and Nd isotopic compositions (Fig. 3.21). The Sr and Nd isotope compositions of the possible dominant end members are also plotted. There could be three potential sources of sediments in the GRS, (i) the Deccan Trap basalts with low ⁸⁷Sr/⁸⁶Sr and high ε_{Nd} ,

(ii) eastern and western Dharwar cratons with high ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and low ε_{Nd} and (iii) eastern gneisses much higher ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and low ε_{Nd} . The isotope compositions of these end members are based on the literature and from this study itself.

On the Sr-Nd isotope mixing diagram (Fig. 3.21), sediments collected from the upstream were dominated by the Deccan basalts, and in the mid and lower basins of the GRS, sediments are sourced from gneisses present the Dharwar cratons.



Fig. 3.21: The binary mixing plot of ε_{Nd} vs. ⁸⁷Sr/⁸⁶Sr in particulate phase of the Godavari River System. The plot suggests that the sediments in the GRS are mixture of three sources, the Deccan basalts, eastern and western Dharwar cratons and eastern gneisses.

3.4 Conclusions

In the present study, we found that the Godavari, Mahanadi and Brahmani Rivers drain into the BoB with an average TDS flux of 20, 4 and 0.75 MT y⁻¹, respectively. In the Godavari River system, Na⁺ and HCO₃⁻ were the most abundant cation and anions in the majority of the samples followed by Ca⁺² and Cl⁻ respectively, whereas, in the Mahanadi and Brahmani Rivers Ca⁺² and HCO₃⁻ were the most abundant cations and anions in all the samples followed by Na⁺ and Cl⁻ which indicates the contribution from chemical weathering along with precipitation and anthropogenic inputs. The upper stream waters of the GRS are higher in TDS values compared to the downstream waters. The chemical weathering in the Godavari, Mahanadi and the Brahmani Rivers deliver the dissolved Sr flux of 124, 22 and 3.6 million moles per annum to the BoB with ⁸⁷Sr/⁸⁶Sr ratio of 0.714642, 0.728543 and 0.731144, respectively.

The silicate erosion rates in the Godavari, Mahanadi and the Brahmani Rivers vary between 4.0 to 22.8, 4.9 to 11.3, and 6.5 to 10.4 tons km⁻² y⁻¹, respectively. The carbonate weathering rates in these rivers vary within the values of 3 - 50, 8.1 - 51.5 and 9.1 - 14.6 tons km⁻² y⁻¹, respectively. The respective CO₂ consumption rates resulting from the silicate weathering in the Godavari, Mahanadi and the Brahmani River basins vary within the range of $(1.2 - 9.0, 0.7 - 2.1 \text{ and } 0.8 - 1.4) \times 10^5 \text{ mol km}^{-2} \text{ y}^{-1}$. The total CO₂ draw-down due to the silicate weathering in the Godavari, Mahanadi and the Brahmani River basins are about (5.23, 1.80 and 0.30) $\times 10^{10} \text{ mol y}^{-1}$, respectively, which account ~0.60, 0.21 and 0.033% of the annual global CO₂ consumption ($870 \times 10^{10} \text{ mol y}^{-1}$).

In the GRS, the dissolved ε_{Nd} displays spatial and temporal variations between -5.2 and -32.8 as a function of the drained lithology. The head waters of the GRS draining Deccan basalts are more radiogenic in ε_{Nd} as compared to the downstream waters, which mostly flow through the Archeans. The chemical weathering in the Godavari River, annually delivers 11.8×10^3 moles of dissolved Nd to the BoB with an average ε_{Nd} of -22.8 respectively.

The ⁸⁷Sr/⁸⁶Sr and ε_{Nd} in the Godavari River sediments vary from 0.708634 to 0.949058 and -4.0 to -37.5, respectively. The sediments of the upper GRS basin, which erodes through the Deccan basalts have more radiogenic ε_{Nd} (-4.0 to -10.6) and less radiogenic ⁸⁷Sr/⁸⁶Sr (0.708634 to 0.714111) whereas, the sediments of the lower basin draining through the cratons contain high radiogenic ⁸⁷Sr/⁸⁶Sr (0.730678 to 0.949058) and less radiogenic ε_{Nd} (-15.0 to -37.5). The

⁸⁷Sr/⁸⁶Sr and ε_{Nd} of sediments of the GRS suggest that the sediments discharged into the BoB are mixture of three sources viz. the Deccan basalts, eastern and western Dharwar cratons and eastern gneisses. It has also been observed that, silicates contribute a minor amount of Sr to the GRS, whereas; weathering of silicates contributes most of ore toutes $ε_{Nd}$ of the GRS. Finally, annually GRS delivers 22.6 and 0.6 M kg of particulate Sr and Nd flux into the BoB with ⁸⁷Sr/⁸⁶Sr and $ε_{Nd}$ of 0.755278 and -27.5, respectively.

Finally, it is concluded that lithology is the primary factor which controls the chemical weathering, and Basalt weathering is faster compared to gneisses. After lithology, runoff seems to have the dominant control on silicate erosion rate. The Godavari and the Mahanadi Rivers contribute a significant amount of dissolved fluxes to the Bay of Bengal and consume the considerable amount of atmospheric CO_2 through silicate weathering, influencing global climate on million years time scale.

Chapter 4

Behavior of Trace Elements and Isotopes in the East Indian Estuaries: Implications to Their Global Marine Budgets

4.1. Introduction

Estuaries act as chemical reactor and help to deliver the dissolved and particulate fluxes brought by rivers into the ocean and serve as reservoir of biogeochemical processes of trace elements. Estuaries regulate the dissolved and particulate fluxes and chemical composition of trace elements and isotopes (TEIs) delivered by rivers to the modern ocean (Church et al., 1996; Windom et al., 2000; Moore, 2010; Rahaman et al., 2010; Rahaman and Singh, 2012; Beck et al., 2013; Rengarajan and Sarma, 2015). Continental inputs, anthropogenic activities and ocean upwelling are the primary sources of nutrients to the surface ocean (Gle et al., 2008). Recent studies recognized that submarine groundwater discharge (SGD) is also a potential source of nutrients and TEIs to the ocean waters (Krest et al., 2000; Windom et al., 2006; Rahaman and Singh, 2012; Beck et al., 2013; Garcia-Orellana et al., 2013; Rengarajan and Sarma, 2015).

Silicate (Si (OH)₄), nitrogen (NO₃¹⁻ and NO₂²⁻), and phosphorus (PO₄³⁻) are the major nutrients, which play an essential role to control the primary production growth of phytoplankton in natural waters. The biogeochemical processes regulate the atmospheric greenhouse gases (CO₂, CH₄, and N₂O; Altabet et al., 2002; Sarma et al., 2010), which regulate the global heat budget. Carbon (C) in marine sediments provides feedback of climate changes. While passing through estuarine gauntlet, concentrations of nutrients and micro-nutrients are modified significantly. Very recent studies have revealed that, SGD is a privileged pathway together with the riverine, anthropogenic and aeolian suppliers of chemical compositions to the marine environments (Kotwicki et al., 2014). The SGD defined as groundwater seepage through continental shelf sediments includes both terrestrial and recycled marine groundwater with emphasis on the coastal zone (Burnett et al., 2003), where the biogeochemical reactions modify the water chemistry (Moore, 2010). The groundwater seepage has been suggested as a potential source of nutrients (Krest et al., 2000), trace metals (Windom et al., 2006), and natural radionuclides (Garcia-Orellana et al., 2013) including Strontium (Sr) to the coastal ocean (Basu et al., 2001; Charette and Sholkovitz, 2006; Paytan et al., 2006; Lin et al., 2010; Moore, 2010; Huang et al., 2011; Johannesson et al., 2011; Rahaman and Singh, 2012; Beck et al., 2013), which leads biogeochemical processes in estuarine and ultimately to the open ocean. The estimation of groundwater seepage into the coastal waters can be obtained with the use of naturally occurring geochemical tracers, which are considered as fingerprint proxies. An advantage of groundwater tracers is that they show an integrated signal while entering into the marine water column via various pathways in the aquifer. Several studies on SGD in the past have used the natural Radium isotopes (²²³Ra, ²²⁴Ra, ²²⁸Ra and ²²⁶Ra) and ²²²Rn to assess the groundwater discharge into the ocean (Burnett et al. 2002, 2003, 2006; Kim and Hwang, 2002; Burnett et al., 2003, 2006; Garcia-Orellana et al., 2014; Rengarajan and Sarma, 2015). A few studies derived the silicate flux through SGD by using ²²⁸Ra and ²²⁶Ra isotopes (Kim et al., 2005; Burnett et al., 2006; Rengarajan and Sarma, 2015). Sr isotope composition of the estuary water has been used recently to track the SGD and associated TEIs fluxes (Rahaman and Singh, 2012). Sr isotope composition (⁸⁷Sr/⁸⁶Sr) in the global seawater is homogenized owing to its longer residence time (\geq 3Myr) in comparison to the ocean mixing time (~1500 yr; Broecker, 1963; Brass, 1976; Burke et al., 1982). Seawater integrates the Sr flux from a variety of sources and display relatively uniform present day Sr concentration (C_{Sr} = ~91.3 µmol kg⁻¹) and ⁸⁷Sr/⁸⁶Sr ratio (0.7092; Palmer and Edmond, 1989; de Villiers, 1999). The temporal variations in the ⁸⁷Sr/⁸⁶Sr ratio in the modern ocean are caused by weathering of various continental rocks, dissolution of carbonates and hydrothermal activities at ocean ridges (Jones and Jenkyns, 2001; Hodell et al., 2007). Therefore, ⁸⁷Sr/⁸⁶Sr of the ocean may provide the essential information on paleo-oceanography like global tectonic and/or climate change events (Colin et al., 1999; Tripathy et al., 2011). The Sr isotopes ⁸⁷Sr and ⁸⁶Sr do not fractionate unlike lighter isotopes (e.g., δ^{13} C, δ^{18} O) by the processes such as phase and chemical speciation, evaporation and biological assimilation. Mixing of Sr from variety of sources leads to change in ⁸⁷Sr/⁸⁶Sr ratio (Goldstein and Jacobsen, 1987; Palmer and Edmond, 1992). Therefore, ⁸⁷Sr/⁸⁶Sr ratios can be used as a proxy in geochemical research and provide us useful information about the mixing of distinct water masses (river water, groundwater, pore-water and seawater) and suspended material. Sr flux from submarine groundwater discharge is poorly constrained. The present study investigated the distributions of dissolved Sr concentrations and isotopic ratios in four eastern Indian estuaries to understand their behavior and flux to the Bay of Bengal (BoB), which is directly relevant to the Sr budget and the evolution of ⁸⁷Sr/⁸⁶Sr in the oceans. The previous studies (Colin et al., 1999; Davis et al., 2003; Allegre et al., 2010; Tripathy et al., 2011) inferred that the Sr isotope composition of paleo seawater archived in marine deposits is being used for stratigraphic correlation, chronology and also to infer about the impact of temporal variability in both tectonics and climate on the isotope evolution. It is, therefore, important to have knowledge about the budget of oceanic Sr and ⁸⁷Sr/⁸⁶Sr along with their sources and sinks in the oceans. The concentration of rare earth elements (REEs) and isotopic composition of Neodymium (ε_{Nd}) serve as important probes to trace the ocean water masses and to comprehend present and paleo-oceanographic circulations, biogeochemical processes and their potential sources like riverine, aeolian, sediments dissolution and hydrothermal activity (Martin et al., 1976; Elderfield and Greaves, 1982; Jeandel, 1993; Sholkovitz and Szymczak, 2000; Rousseau et al., 2015). Several studies revealed the behavior of dissolved REE concentrations in estuaries and recognized that the REEs are removed from the dissolved phase in the low salinity zones and partially released back at mid to high salinity regions (Martin et al., 1976; Hoyle et al., 1984; Goldstein and Jacobsen, 1988b, c; Elderfield et al., 1990; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000; Rousseau et al., 2015). The removal of trace elements (e.g. Fe, Mn and REEs) from the mixing zones could be due to coagulation of river colloids in low salinity zones, adsorption of trace elements onto the suspended particulates and/or on Fe-Mn oxy-hydroxides, destabilization of mixed iron oxideorganic matter colloids during mixing with seawater. The release and re-supply of the trace elements are attributable to dissolution and/or desorption of SPM, Fe-Mn oxyhydroxides and through SGD (Coonley et al., 1971; Sholkovitz, 1976; Yeats and Bewers, 1976; Boyle et al., 1977; Sholkovitz and Szymczak, 2000; Kim and

Kim, 2014; Rousseau et al., 2015). This release of dissolved REEs could be globally important in terms of their missing source flux and the inter-ocean differences in the Nd isotopic composition of seawater.

The objective of the present study is to examine the behavior of selected trace elements such as Sr, REEs and Mn along with the isotope compositions of Sr and Nd during high water discharge period in the east flowing estuaries of India namely the Ganga (Hooghly), Mahanadi, Krishna and the Godavari. Impact of submarine discharge, particle-water interaction and oxic/redox condition of these estuaries in controlling the distribution of these trace elements in these estuaries has been evaluated. Fluxes of these elements and isotopes from these estuaries to the BoB from the various sources such as riverine, SGD, and particle release have been estimated in this study. An attempt is also made to assess the role of these fluxes in contributing to their global oceanic budgets. For the first time, the chemical compositions of dissolved REEs, dissolved Manganese (Mn) and ε_{Nd} of dissolved and particulate phases in these estuaries are studied.

4.2. Results

Water and sediment samples were collected from the Ganga, Mahanadi, Krishna and the Godavari estuaries during monsoon, 2013. The locations are listed in the Chapter-2 along with the date of collection, salinity (S), temperature (T), pH and dissolved Oxygen (DO) of the water samples (Table 2.8; Fig. 2.5).

In-situ measurements were carried out of the general parameters such as pH, salinity and temperature in the surface waters from the above estuaries. Dissolved Oxygen is estimated on board ORV Sagar Manjusha (SM-24-13) in the water samples immediately after their collection from the Ganga estuary. The concentration of major and trace elements, 87 Sr/ 86 Sr and ϵ_{Nd} were measured in waters from these estuaries to examine their behavior, the potential sources and contribution of the TEIs to the global marine budget. The abundances of major elements, Sr and Nd and 87 Sr/ 86 Sr and ϵ_{Nd} in sediments from these estuaries were also quantified to understand their behavior in these mixing zones. Physical

parameters of these rivers have been listed in Table 4.1, which helps calculate the dissolved and particulate chemical fluxes to the ocean.

Table 4.1: Drainage area, annual water and sediment discharge and runoff of theGanga, Mahanadi, Krishna and the Godavari Rivers

River	Drainage Area	Discharge	SPM	Runoff
	10^6 km ²	$10^{14} \mathrm{L y^{-1}}$	10 ¹⁴ g y ⁻¹	mm. y ⁻¹
Ganga	0.935	3.80	4.18	470
Mahanadi	0.132	0.66	0.60	500
Krishna	0.259	0.30	0.64	116
Godavari	0.303	1.05	1.70	335

All data from the compilation of Biksham and Subramanian, 1988a, and b; Trivedi et al., 1995; Galy et al., 1999; Singh et al., 2008.

4.2.1 Dissolved Sr and ⁸⁷Sr/⁸⁶Sr

The dissolved Sr concentrations and 87 Sr/ 86 Sr ratios measured at various salinity zones of the Ganga, Mahanadi, Krishna and the Godavari have been provided in Table 4.2. The riverine end members of Sr concentrations and 87 Sr/ 86 Sr ratios are 0.99, 3.09 and 1.26 µmol kg⁻¹ and 0.718197, 0.713915 and 0.714524 in the Mahanadi, Krishna and the Godavari Rivers respectively at zero salinity which reflects the lithology they drain such as gneissic/cratonic signature of the Mahanadi source area, and the combination of the Deccan basalts and gneissic rocks signatures for the Krishna and Godavari source areas. However, water sample could not be collected in the Ganga estuary at zero salinity due to logistic reasons. Therefore, we have considered the values of Sr concentration and its isotope ratio at the zero salinity of the Ganga River measured at Manihari during monsoon, which are 0.885 ± 0.04 µmol kg⁻¹, and 0.73132 ± 0.0009% respectively (Chatterjee, 2013). The dissolved Sr concentrations and isotope ratios at different salinities from the Ganga mixing zone were measured in the present study (Table 4.2).

Table 4.2: Salinity, dissolved Sr concentrations, and ⁸⁷Sr/⁸⁶Sr ratio in the Ganga, Mahanadi, Krishna, and Godavari estuaries.

Sample ID	Location	Salinity	Sr	±	⁸⁷ Sr/ ⁸⁶ Sr	±
	code		µmol Kg ⁻¹	_		
Ganga Estuary						
BR10 35	H-0	0.0	0.885	0.04	0.73132	0.000009
Hooghly-13/02	H-2	0.3	1.73	0.04	0.719794	0.000013
Hooghly-13/01	H-1	0.4	2.05	0.02	0.718275	0.000005
SM-24-13/01	H-3	3.8	10.01	0.14	0.710822	0.000009
SM-24-13/02	H-4	4.8	11.98	0.37	0.710482	0.000020
SM-24-13/03	H-5	6.5	16.97	0.14	0.710124	0.000010
SM-24-13/04	H-6	7.8	19.20	0.30	0.709947	0.000008
SM-24-13/05	H-7	9.7	23.70	0.25	0.709773	0.000008
SM-24-13/06	H-8	11.3	28.57	0.17	0.709666	0.000008
SM-24-13/07	H-9	13.8	33.76	0.21	0.709538	0.000010
SM-24-13/08	H-10	18.6	45.46	0.16	0.709427	0.000008
SM-24-13/09	H-11	21.3	51.12	0.32	0.709359	0.000009
SM-24-13/10	H-12	23.3	57.19	0.14	0.709286	0.000007
SM-24-13/11	H-13	19.1	45.24	0.27	0.709317	0.000011
SM-24-13/12	H-14	29.4	70.83	0.19	0.709223	0.000010
Mahanadi Estuar	У					
MND-13/01	M-1	0.0	0.99	0.20	0.718197	0.000008
MND-13/02	M-2	0.1	1.35	0.02	0.716591	0.000007
MND-13/03	M-3	0.2	1.84	0.02	0.714613	0.000009
MND-13/04	M-4	0.4	2.04	0.04	0.713943	0.000010
MND-13/05	M-5	2.8	7.51	0.11	0.710415	0.000012
MND-13/06	M-6	23.7	56.23	0.37	0.709226	0.000013
MND-13/07	M-7	26.0	62.59	0.17	0.709262	0.000007
MND-13/08	M-8	26.4	64.18	0.15	0.709236	0.000010
MND-13/08-35m	M-8	n.a	76.36	0.17	0.709195	0.000014
MND-13/09	M-9	32.4	64.53	0.29	0.709245	0.000012
MND-13/09-35m	M-9	n.a	78.46	0.13	0.709218	0.000008
Krishna Estuary						
KR-13/01	K-1	0.0	3.09	0.04	0.713915	0.000009
KR-13/02	K-2	0.5	4.10	0.07	0.713147	0.000008
KR-13/03	K-3	1.9	7.32	0.05	0.711420	0.000006
KR-13/04	K-4	2.7	8.94	0.14	0.710974	0.000012
KR-13/05	K-5	4.0	12.36	0.19	0.710433	0.000016
KR-13/06	K-6	5.1	14.40	0.16	0.710255	0.000014
KR-13/07	K-7	6.9	18.81	0.10	0.709962	0.000007
KR-13/11	K-11	10.3	26.43	0.29	0.709665	0.000040
KR-13/10	K-10	14.6	36.96	0.13	0.709531	0.000007
KR-13/09	K-9	18.1	44.52	0.11	0.709409	0.000010
KR-13/08	K-8	30.2	74.03	0.04	0.709233	0.000017
Godavari Estuary	7					
GDV-13/18	G-1	0.0	1.26	0.07	0.714524	0.000022
GDV-13/19	G-2	1.6	5.06	0.04	0.710569	0.000007

GDV-13/20	G-3	2.8	7.67	0.05	0.710152	0.000008
GDV-13/21	G-4	5.1	13.25	0.08	0.709721	0.000009
GDV-13/22	G-5	6.4	16.05	0.15	0.709615	0.000008
GDV-13/23	G-6	10.0	24.74	0.15	0.709430	0.000007
GDV-13/24	G-7	12.2	30.34	0.13	0.709392	0.000011
GDV-13/25	G-8	15.0	36.90	0.18	0.709338	0.000007

n.a: Not analyzed

4.2.2 Major ions in estuarine waters

The work presented here includes the measurement of concentration of nutrients viz. nitrate and silicate. The concentrations of major ions in these estuaries are listed in Table 4.3. The mean silicate values in the Ganga, Mahanadi, Krishna and the Godavari estuaries are 80, 60, 193 and 263 μ M respectively (Table 4.3). Due to lower abundances of Nitrate (NO₃⁻), we could measure its concentration in a few samples in these estuaries as listed in Table 4.3. The concentration of total dissolved solids (TDS) in these estuaries varies from 408 to 27660, 187 to 26624, 359 to 28753 and 200 to 14300 mg L⁻¹ respectively (Table 4.3) in the Ganga, Mahanadi, Krishna and the Godavari estuaries. These results emphasize that the major ionic composition in these mixing zones are mostly controlled by seawater.

4.2.3 REEs and ϵ_{Nd} behavior in East Indian estuarine waters

The measured concentrations of REEs and Nd isotopic compositions in East Indian estuarine waters have been listed in Table 4.4. The dissolved REEs display two distinct characteristics in the Ganga, Mahanadi and the Krishna mixing zones. The distribution of REEs with salinity indicates their removal in low salinity zone (S = 0.5) and moderate to extensive release in the mid and high salinity zones of all the estuaries (Fig. 4.1a-d and 4.2a-d) compared to the respective riverine fresh waters.

In the Ganga estuary, The REE- salinity distribution indicates a moderate removal of dissolved REEs in low salinity zone (S = 0.5) and moderate to extensive release in the mid and high salinity zones and there is no removal observed for La, Pr, Tb and all HREEs in low salinity zone. The removal of

LREE (38-88%) is greater than that of MREE (20-80%) from the Ganga Riverine fresh waters. However, the release of REEs is observed in a descending order, LREE (1-150 times) > MREE (7-70 times) > HREE (1-50 times), (Fig. 4.1a and 4.2a). In the Ganga estuary, the dissolved Nd concentration lies between 20.4-3069 pmol kg⁻¹ and ϵ_{Nd} varies between -14.7 and -13.9 (Table 4.4). Here, particulate Nd concentrations varies between 14.0 and 16.4 µg g⁻¹ and their ϵ_{Nd} vary from -18.5 to -15.3 at various salinities (S = 0.3 to 23.3; Table 4.5).

In the Mahanadi mixing zone, the REE – salinity distribution indicates a sharp removal of dissolved REEs near very low salinity (0-0.5) zone and moderate release in the mid to high salinity zones (Fig. 4.1b, 4.2b). The Fig. 4.1b and 4.2b shows the order of removal as LREE (50-80%), MREE (30-60%), HREE (20-80%) and the order of release as HREE (0.2-1.8 times), MREE (0.3-1.8 times), LREE (0.2-1.0 times). The dissolved Nd concentration and ε_{Nd} in the Mahanadi estuarine waters exist between 37.4 and 165 pmol kg⁻¹ and -23.6 and -13.2 respectively (Table 4.4).

In the Krishna estuary, the REE – Salinity distribution demonstrates a gentle removal of dissolved REEs near the low salinity (0-5) zone and considerable release in the mid to high salinity zones (Fig. 4.1c, 4.2c). There is no such removal observed for La in low salinity zone. The order of removal follows as LREE (10-80%), MREE (~10%), HREE (~6%) and the order of release follows LREE (0.7-8.0 times), MREE (0.8-6.0 times), HREE (1-3 times; Fig. 4.1c, 4.2c). The dissolved Nd concentration and ε_{Nd} in the Krishna estuarine waters vary from 37.3 to 333 pmol kg⁻¹ and from -15.4 to -11.4 respectively (Table 4.4). However, in the Krishna estuary particulates have very low Nd concentration of 2.89 µg g⁻¹ and its isotopic composition (ε_{Nd}) of -23.5 (Table 4.5).

Sample ID	Salinity	Na^+	\mathbf{K}^+	Ca ²⁺	Mg^{2+}	Cl	SO ₄ ²⁻	Br	NO ₃	SiO ₂	Alk.	NICB	TDS
						μM						%	mg L ⁻¹
Ganga Estuary													
Hooghly-13/02	0.3	3578	161	728	633	3291	341	b.d	b.d	60	1990	8.37	408
Hooghly-13/01	0.4	5248	194	750	811	5093	455	b.d	b.d	72	1926	8.00	524
SM-24-13/01	3.8	49556	1107	1605	5671	51132	3363	576	850	110	1945	6.51	3745
SM-24-13/02	4.8	61122	1330	1847	6992	65062	4026	630	b.d	97	1935	5.88	4569
SM-24-13/03	6.5	89024	1909	2404	10042	91334	5836	1027	b.d	108	1938	9.30	6467
SM-24-13/04	7.8	101809	2082	2637	11396	105677	6640	1157	b.d	159	1948	8.11	7410
SM-24-13/05	9.7	25502	520	626	2846	26337	1673	b.d	b.d	94	1950	4.21	1920
SM-24-13/06	11.3	141900	3012	3560	16696	151655	8903	b.d	b.d	92	1959	8.17	10469
SM-24-13/07	13.8	166922	3599	4109	19761	176645	10273	1742	2135	83	1990	7.49	12500
SM-24-13/08	18.6	241765	4760	5427	26843	266779	14083	1453	1637	98	1992	3.68	17770
SM-24-13/09	21.3	279908	5487	6188	31199	287565	16940	2694	b.d	51	2028	10.42	19820
SM-24-13/10	23.3	311653	6202	6885	34938	322839	18783	2975	b.d	18	2022	9.88	22145
SM-24-13/11	19.1	230471	5026	5555	28043	246558	14620	2467	b.d	26	1808	8.08	17314
SM-24-13/12	29.4	379305	7946	8622	44857	397056	23180	3743	b.d	37	2113	10.00	27660
Mahanadi Estu	ary												
MND-13/01	0.0	1126	75	425	267	854	109	14	30	107	1391	3.10	187
MND-13/02	0.1	2901	105	440	480	2628	192	17	29	108	1378	9.24	305
MND-13/03	0.2	6577	179	471	848	6653	393	34	b.d	108	1379	6.13	565
MND-13/04	0.4	7791	213	526	999	7809	540	89	b.d	104	1379	6.73	659

Table 4.3: The concentrations of major ions from the East Indian estuaries along with the normalized inorganic charge balance and total dissolved salts in mg L^{-1} .

MND-13/05	2.8	35040	775	1095	3975	36846	2399	458	b.d	101	1383	5.68	2640
MND-13/06	23.7	307407	6465	6835	34362	322901	20230	3625	b.d	6	1630	7.50	22210
MND-13/07	26.0	359194	8830	7881	28181	370918	21108	3108	4094	3	1985	4.22	25405
MND-13/08	26.4	372535	9654	8931	30049	376699	21768	3404	4460	3	1994	6.99	26469
MND-13/09	32.4	375943	10286	9740	32759	380496	22483	3816	4954	4	2151	7.98	26624
Krishna Estuar	У												
KR-13/01	0.0	2779	88	600	586	1776	448	13	35	209	2150.5	7.55	359
KR-13/02	0.5	7603	178	739	960	7199	712	36	65	220	1750	6.74	685
KR-13/03	1.9	24931	563	1111	2583	25416	1638	137	b.d	213	1844.5	7.20	1897
KR-13/04	2.7	33420	761	1350	3382	35225	2164	190	b.d	220	1795.5	5.07	2529
KR-13/05	4.0	51436	1137	1775	5225	53991	3104	281	b.d	212	1809.5	6.88	3783
KR-13/06	5.1	63910	1394	1976	6505	68549	3855	349	b.d	215	1862	4.84	4716
KR-13/07	6.9	89256	1919	2494	9254	96033	5188	480	537	242	1750	5.03	6548
KR-13/11	10.3	131818	2827	3293	13670	143363	7654	701	b.d	51	1638	4.70	9582
KR-13/10	14.6	190416	4057	4539	19796	208401	10945	977	b.d	174	1890	4.28	13843
KR-13/09	18.1	205771	4298	5313	21696	216378	11586	1209	b.d	166	1659	8.94	14631
KR-13/08	30.2	402093	8484	9042	41904	433086	22380	2146	b.d	196	1795.5	6.37	28753
Godavari Estua	ry												
GDV-13/18	0.0	482	48	599	307	222	76	b.d	55	292	2017	-4.20	203
GDV-13/19	1.6	49054	1475	1813	4676	55944	2981	258	b.d	276	1659	-0.49	3780
GDV-13/20	2.8	36909	997	1653	3599	43109	2382	214	b.d	285	1823	-3.01	2944
GDV-13/21	5.1	68763	1922	2017	7075	83533	4349	385	b.d	270	2089	-6.16	5462
GDV-13/22	6.4	84611	2108	2407	9085	102911	5211	466	b.d	270	1930	-5.21	6665
GDV-13/23	10.0	132682	3372	3524	14083	158290	8215	747	b.d	250	2104	-3.55	10270
GDV-13/24	12.2	164793	4047	4211	17731	199564	10022	894	b.d	234	2166	-4.47	12802
GDV-13/25	15.0	178796	3990	6476	18689	225831	11321	1131	b.d	231	2273	-7.45	14317

ID	Sal.	Mn	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	¹⁴³ Nd/ ¹⁴⁴ Nd	E _{Nd}
Ganga	Estuary	y																
H-0	0.0	b.d.	8.0	82.9	1.9	65.3	38.5	4.7	26.0	1.1	17.7	1.6	11.3	0.7	10.0	0.7	0.511813#	-16.1
H-02	0.3	4.15	17.8	23.3	5.1	27.7	6.9	2.0	14.2	1.6	14.0	2.5	11.6	1.0	11.2	1.1	0.511916	-13.9
H-01	0.4	3.00	18.9	20.2	4.9	30.4	8.3	2.3	16.1	1.7	15.0	2.8	13.9	1.2	13.0	1.2	0.511902	-14.2
H-03	3.8	4.10	28.7	19.6	6.4	30.4	8.4	2.7	14.3	2.4	18.2	4.5	14.8	2.2	15.0	2.3	0.511911	-14.0
H-04	4.8	4.11	16.9	9.7	4.2	20.4	6.4	2.1	11.7	2.0	16.1	4.2	15.5	2.3	15.9	2.3	0.511895	-14.3
H-05	6.5	8.20	38.0	27.9	9.0	40.6	10.9	3.3	15.6	2.9	21.3	5.4	19.2	2.6	17.3	2.6	0.511883	-14.6
H-06	7.8	1985	3801	7066	858	3069	817	181	940	121	649	112	291	37.8	222	33.6	0.511878	-14.7
H-07	9.7	24.28	114.1	123.0	25.0	104.0	19.1	5.5	18.4	3.1	17.0	3.2	11.7	1.3	9.5	1.3	0.511894	-14.4
H-08	11.3	2.34	20.6	11.6	5.0	24.5	7.1	2.7	12.0	2.7	21.8	5.8	19.0	2.8	19.0	2.8	0.511919	-13.9
H-09	13.8	6.35	22.5	17.3	5.5	27.9	9.1	3.1	20.1	3.0	24.6	6.5	22.6	3.1	20.8	3.0	0.511892	-14.4
H-10	18.6	11.03	53.1	77.1	15.9	69.2	16.8	4.8	21.8	3.1	20.2	4.4	13.5	1.9	12.6	1.8	0.511879	-14.6
H-11	21.3	20.10	25.6	28.5	7.6	37.6	11.0	3.8	20.1	4.1	32.9	8.5	27.4	4.1	27.3	4.1	0.511922	-13.8
H-12	23.3	39.36	17.3	27.7	5.4	29.1	8.7	3.1	16.6	3.4	28.1	7.2	24.1	3.5	22.0	3.3	0.511883	-14.6
H-13	19.1	18.88	25.2	27.5	7.3	35.2	11.3	3.6	19.9	3.6	29.4	7.5	25.5	3.3	21.7	3.1		
Mahan	adi Est	uary																
M-01	0.0	4.73	180.0	194.0	30.1	165.0	37.2	9.9	61.5	19.0	33.2	26.1	25.1	7.7	20.3	14.4	0.511474	-22.7
M-02	0.1	1.55	53.8	54.7	5.4	59.5	14.0	4.1	20.8	11.1	18.6	14.1	13.8	2.8	12.8	6.2	0.511430	-23.4
M-03	0.2	14.43	74.8	85.0	16.6	79.9	19.4	4.7	26.0	3.8	21.9	5.7	16.0	2.0	14.6	2.1	0.511419	-23.6
M-04	0.4	4.97	73.1	64.9	14.8	74.0	17.2	4.8	28.1	4.1	22.7	6.1	17.1	2.3	15.6	2.7	0.511452	-23.0
M-05	2.8	60.51	130.0	118.0	27.9	118.0	23.1	5.3	19.3	4.6	30.6	7.3	22.7	3.2	19.0	2.9	0.511424	-23.5

Table 4.4: The concentration of dissolved Mn (nmol kg^{-1}) and REEs (pmol kg^{-1}) and isotope composition of Nd in all the estuarine samples along with their salinity (Sal.) from the present study

M-06	23.7	18.66	164.0	105.0	30.3	133.0	29.3	9.1	29.8	7.8	59.0	14.7	45.6	6.7	40.5	5.9	0.511490	-22.2
M-07	26.0	11.55	37.8	44.7	12.5	60.0	18.5	6.1	36.2	6.2	47.5	11.7	35.8	5.0	31.4	4.6	0.511910	-14.2
M-08	26.4	6.98	34.6	32.7	10.1	51.6	14.8	5.3	26.1	5.2	40.4	10.1	28.0	4.0	25.5	3.7	0.511853	-13.5
M-09	32.4	7.70	39.2	38.1	9.6	45.5	14.4	4.7	21.4	4.6	36.3	8.9	25.4	3.6	22.4	3.3	0.511954	-13.2
Krishn	a Estua	ry																
K-01	0.0	0.67	29.0	33.9	9.6	46.2	12.1	4.4	22.7	2.6	20.2	5.0	16.9	2.1	14.4	2.0	0.511849	-15.4
K-02	0.5	b.d.	33.3	15.5	8.3	41.3	10.7	4.0	18.5	2.4	19.8	4.7	16.3	2.0	14.0	1.9	0.511847	-15.4
K-03	1.9	b.d.	32.7	7.2	7.9	37.4	10.8	3.7	18.3	2.5	20.6	4.9	17.2	2.3	14.8	2.1	0.511847	-15.4
K-04	2.7	0.34	33.0	30.6	9.6	47.6	12.3	4.3	18.5	2.9	21.7	5.7	18.9	2.7	16.0	2.5	0.511842	-14.0
K-05	4.0	2.24	21.6	38.1	7.8	37.3	10.7	4.0	18.8	3.1	23.9	5.8	18.4	2.6	16.3	2.5	0.512052	-11.4
K-06	5.1	7.01	37.2	55.5	12.3	58.7	14.2	5.6	23.7	3.8	27.5	6.7	23.2	2.9	17.5	2.7	0.511942	-13.6
K-07	6.9	89.61	195.0	230.0	76.9	333.0	76.6	20.2	72.8	11.3	67.4	13.7	42.8	5.6	32.5	4.5	0.511939	-13.6
K-11	10.3	42.31	44.3	72.5	13.3	63.5	18.2	6.8	27.1	4.6	33.8	8.3	25.6	3.4	20.4	3.1	0.511940	-13.6
K-10	14.6	38.47	57.6	83.9	18.0	86.3	19.5	7.3	29.2	4.8	35.3	8.4	29.3	3.7	22.2	3.3	0.511862	-15.1
K-09	18.1	21.83	52.9	60.7	15.6	75.6	20.2	7.9	34.7	5.5	39.6	9.9	31.1	4.2	24.3	3.6	0.511956	-13.3
K-08	30.2	14.81	52.8	88.5	17.4	80.6	19.3	6.8	36.4	4.9	36.6	8.9	26.5	3.8	22.3	3.6	0.512022	-12.0
Godava	ari Estu	ary																
G-01	0.0	b.d.	65.5	43.8	16.4	72.6	18.0	6.0	22.6	3.1	22.0	5.1	16.5	1.9	12.9	1.7	0.511701	-18.3
G-22	1.6	10.79	87.4	64.3	19.2	87.7	19.7	6.2	28.2	3.8	27.4	6.4	20.7	2.4	15.1	2.3	0.511564	-20.9
G-03	2.8	17.33	69.1	90.0	22.3	105.0	26.4	7.2	32.5	4.6	31.6	7.1	22.7	3.1	18.6	2.8	0.511535	-21.5
G-04	5.1	19.43	225.0	158.0	45.5	186.0	35.2	10.0	42.5	6.0	41.3	9.7	29.8	4.1	23.2	3.6	0.511451	-23.2
G-05	6.4	43.13	167.0	92.8	32.5	138.0	31.6	9.1	41.1	6.0	40.0	9.5	31.0	4.1	24.0	3.4	0.511521	-21.8
G-06	10.0	59.88	258.0	138.0	44.5	184.0	33.0	10.7	45.7	6.5	44.4	10.5	32.8	4.4	26.5	3.9	0.511524	-21.7
G-07	12.2	50.52	251.0	131.0	42.9	178.0	40.3	11.7	57.8	8.3	56.2	13.2	37.5	5.2	30.0	4.5	0.511541	-21.4
G-08	15.0	b.d.	414.0	340.0	78.7	311.0	54.3	16.1	70.5	10.5	68.6	15.9	47.9	6.3	34.6	5.1	0.511390	-24.4

#: Sampling details and ¹⁴³Nd/¹⁴⁴Nd (ε_{Nd}) data available in Chatterjee, 2013; **b.d.:** Below detection



Fig. 4.1 (a-d): Plot of dissolved REEs vs. salinity in the eastern Indian estuaries. The plots show the removal/release of REEs with salinity gradient in the Ganga, Mahanadi, Krishna and the Godavari estuaries.



Fig. 4.2 (a-d): Plot showing the distribution pattern of river normalized REEs vs. salinity in the eastern Indian estuaries. The plot indicates that removal of REEs at low salinity zones and their release at mid to high salinity zones occurs in the Ganga, Mahanadi, Krishna and the Godavari estuaries.

In the Godavari estuary, the behavior of dissolved REEs is unique as compared to the other three estuaries. A continuous enrichment has been observed in the dissolved REEs with salinity gradient in this estuary (Fig. 4.1d, 4.2d). The order of enrichment follows as LREE (1.2-8.0 times), MREE (0.8 to 3.0 times) and HREE (1-3 times; Fig. 4.1d, 4.2d) with increasing salinity. The respective dissolved Nd concentrations and ε_{Nd} in the Godavari estuarine waters vary between 72.6 and 311 pmol kg⁻¹ and -24.4 to -18.3, respectively (Table 4.4). In the Godavari estuary, only a few of particulates have been examined for Nd concentrations and isotopic compositions. The Nd concentrations in silicate fractions are 12.6 and 5.1 µg g⁻¹ and ε_{Nd} values are -7.45 and -27.07 in the sediments collected at salinities of 0 and 4.5 (Table 4.5).

4.2.4 Concentration of major elements, Sr - Nd, and $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵ_{Nd} in sediments

The abundances of major elements (Na, K, Ca, Mg, Al, Fe, Mn, Ti), Sr and Nd and isotope ratios of Sr and Nd have been analyzed in the silicate fraction of the sediments from the Ganga, Krishna and the Godavari estuaries (Table 4.5). The relative abundances of these elements in the shelf sediments have been observed in order, $Al > Fe > K \ge Mg > Ca > Na > Ti > Mn$, which originate in large extent from the Earth's crust through physical and/or chemical weathering. Al is the most abundant in most of the samples followed by Fe. Al varies from 6.9 to 9.2, 3.4 to 4.6 and 3.6 to 7.2 wt % in the sediments of the Ganga, Krishna and the Godavari mixing zones respectively (Table 4.5). The respective chemical index of alteration (CIA = $[Al_2O_3/(Na_2O + K_2O + CaO + CaO$ Al_2O_3] × 100; Nesbitt and Young, 1982) in the Ganga, Krishna and the Godavari estuaries varies between 73 and 79, 50 and 54 and 55 and 75%, respectively (Table 4.5). Sr concentrations and its isotope ratios have been determined in silicate fractions of the bedload/suspended sediments from these estuaries. SPM content was quite low in the low salinity zone of the Ganga estuary. In the mid salinities (3-6), the amount of SPM enhanced drastically (Table 4.5; Fig. 4.3). This rapid enrichment of SPM in mid salinities is about 16
times higher than its concentration at lower salinity (S=0.3), which could be due to re-suspension of bottom sediments and colloidal matters by the turbulent estuarine tidal forces (Ward et al., 1984; Jeandel, 2016). This rapid enrichment of the SPM decreases rapidly and followed by a continuous depletion towards the high salinities in the Ganga estuary. In the higher salinities at S = 18, SPM again marginally increased and followed by its depletion. In the Ganga estuary, particulate Nd concentration and ε_{Nd} values show a coherent relation with the SPM concentration (Fig. 4.3a, b). However, particulate Sr and ⁸⁷Sr/⁸⁶Sr inversely related with the SPM concentrations along with the salinity gradient (Fig. 4.3a, b).



Fig. 4.3: The plots show the variations of (a) suspended particulate matter (SPM), Sr and Nd abundances in SPM and (b) 87 Sr/ 86 Sr and ε_{Nd} in SPM along with the salinity gradient in the Ganga estuary.

The typical Sr concentration and isotopic composition of SPM of the Ganga estuary lie between 42.9 to 61.8 μ g g⁻¹ and 0.757621 to 0.766794 respectively. These values are similar to the reported Sr concentration and its isotope ratios present in the silicate fraction of the Ganga River bank sediments, which vary from 38 to 138 μ g g⁻¹ and 0.75527 to 0.78652 respectively (Singh et al., 2008). The Sr concentration and ⁸⁷Sr/⁸⁶Sr ratios in one of the SPM from the Godavari estuary are of 75 μ g g⁻¹ and 0.731446 respectively. The respective Sr concentrations and ⁸⁷Sr/⁸⁶Sr ratios are 200 μ g g⁻¹ and 0.739268 in the Krishna and 120-156 μ g g⁻¹ and 0.745686-0.746990 in the Godavari estuaries (Table 4.5). Nd concentrations and its isotope ratios in the silicate fraction of the sediments from these estuaries are also mentioned in Table 4.5.

4.2.5 pH, dissolved Oxygen and dissolved Mn in East Indian Estuaries

In the present study, the pH values of the estuary waters vary from 7.70 to 8.49. The relative pH values in these estuaries observed in order of the Krishna > Godavari > Mahanadi \geq Ganga which are listed in Chapter-2 (Table 2.8). Measured DO in the Ganga estuary has also been mentioned in the Chapter-2 (Table 2.8). The DO ranges from 122 to 139 (\pm 4) μ M. There are two depleted DO values (127 and 122 µM) observed at mid (S=7.8) and high (S=29.4) salinities respectively. The dissolved Mn concentrations of the Ganga, Mahanadi, Krishna and the Godavari estuary are listed in Table 4.4 and plotted in Fig. 4.4a-d. In the Ganga, Mahanadi and the Krishna estuary the dissolved Mn is removed from the surface waters at low salinity zones and it is maximum at mid and high salinities. The respective removal of dissolved Mn at low salinity zones is 28% (S = 0.4), 77% (S = 0.1) and 50% (S = 2.7) in the Ganga, Mahanadi and the Krishna estuaries. However, in the Godavari estuary, the dissolved Mn gradually increases with salinity (Fig. 4.4d). The dissolved Mn of the Ganga estuarine samples has been normalized by the Mn content measured at S = 0.3. However, the dissolved Mn in the Mahanadi, Krishna and the Godavari estuary samples are normalized by Mn at S = 0. In all these estuaries, in the mid to high salinities (5-33.4) dissolved Mn is released to the estuarine waters. This release is moderate to extensive. The order of enrichment of dissolved Mn in the Ganga, Mahanadi, Krishna and the Godavari estuaries is 1-480, 1-16, 3-130 and 8-40 times respectively, with respect to their river end-member dissolved Mn.

Sample ID	SPM	Na	K	Ca	Mg	Al	Fe	Ti	Mn	Sr	Nd	⁸⁷ Sr/ ⁸⁶ Sr	¹⁴³ Nd/ ¹⁴⁴ Nd	E _{Nd}	CIA
	$g L^{-1}$				wt%				-	$\mu g g^{-1}$	l				
Ganga Estuary															
Hooghly-13/01	0.098	0.63	2.20	0.58	1.74	7.20	5.49	0.49	205	59	14.5	0.766642	0.511731	-17.7	73
Hooghly-13/02	0.124	0.67	2.28	0.66	1.81	7.47	5.63	0.50	179	62	15.1	0.766794	0.511711	-18.1	73
SM-24-13/01	1.515	0.64	1.78	0.65	2.09	8.39	6.85	0.61	278	53	16.3	0.761843	0.511824	-15.9	78
SM-24-13/02	1.175	0.64	1.82	0.6	2.07	8.55	6.81	0.60	282	47	16.4	0.760862	0.511841	-15.5	78
SM-24-13/03	1.661	0.59	2.34	0.65	2.04	8.15	6.71	0.62	281	46	15.3	0.758587	0.511811	-16.1	75
SM-24-13/04	0.841	0.53	1.95	0.53	1.66	6.87	6.81	0.63	308	58	15.7	0.759990	0.511691	-18.5	75
SM-24-13/05	0.914	0.5	2.38	0.58	2.24	8.68	7.74	0.63	298	43	15.3	0.758154	0.511853	-15.3	77
SM-24-13/06	0.615	0.52	2.35	0.62	2.16	8.26	6.82	0.61	276	50	15.5	0.760173	0.511824	-15.9	76
SM-24-13/07	0.353	0.52	1.72	0.56	1.93	8.08	7.37	0.60	252	51	14.0	0.759769	0.511814	-16.1	79
SM-24-13/08	0.503	0.52	2.35	0.61	2.13	8.39	7.48	0.63	311	43	16.1	0.757758	0.511773	-16.9	76
SM-24-13/09	0.206	0.54	2.36	0.60	2.19	8.34	7.14	0.62	296	54	15.0	0.757737	0.511764	-17.1	76
SM-24-13/10	0.165	0.62	2.39	1.06	2.47	9.24	6.98	0.60	80	45	16.2	0.757621	0.511785	-16.6	75
Krishna Estuary	7														
KR-13/01-BL		1.09	1.69	2.44	1.43	4.61	7.86	2.40	621	207	2.89	0.739268	0.511434	-23.5	53
Godavari Estuar	ry														
GDV-13/18	0.105	0.64	1.01	1.33	1.6	7.19	8.84	1.08	343	75	12.6	0.731446	0.511744	-17.4	75
GDV-13/25-SS		0.99	1.90	1.60	0.88	4.42	2.76	0.47	126	156	5.1	0.745686	0.511250	-27.1	55

Table 4.5: The amount of SPM, particulate Sr, Nd concentrations and their isotope ratios in estuarine samples from the present study along with their major elements abundances

SPM: Suspended particulate matter, BL: bed/bank load sediment, SS: Surface slurry



Fig. 4.4: The plots (a-d) show the distribution patterns of dissolved Mn in the East Indian estuaries.

4.3. Discussion

4.3.1. Behavior of dissolved Sr and ⁸⁷Sr/⁸⁶Sr in mixing zone and their applications to SGD

4.3.1.1 Behavior of dissolved Sr concentration in the East Indian estuaries

The variations of dissolved Sr concentration with salinity in the Ganga, Mahanadi, Krishna and the Godavari estuary have been shown in Fig. 4.5a-d. It is clear from the Fig. 4.5a-d, that there are strong conservative mixing between riverine and marine sources of which is substantiated by the very high positive correlation coefficient, R^2 , ~1.00. All the dissolved Sr data in these estuaries show the linear correlation with salinity i.e. they fall on the mixing line defined by river and seawater end-member. The intercepts of the best fit lines of these plots are found to be 0.95 ± 0.25 , 1.08 ± 0.22 , 2.73 ± 0.16 and 1.11 ± 0.11 , respectively, in the Ganga, Mahanadi, Krishna and the Godavari estuary waters. These values are close to their corresponding dissolved Sr concentrations measured at zero salinity (Table 4.2; Fig. 4.5a-d). These linear variations of the dissolved Sr concentrations with the salinity conclude that the dissolved Sr in these estuaries is mainly controlled by the seawater and the river water input without any other potential source in the estuary.



Fig. 4.5: Dissolved Sr vs. salinity plots of the (a) Ganga (Hooghly), (b) Mahanadi, (c) Krishna and the (d) Godavari estuaries. In all four estuaries, Sr shows conservative nature.

4.3.1.2 Behavior of dissolved ⁸⁷Sr/⁸⁶Sr in mixing zone

The behavior of the dissolved Sr with salinity (Fig. 4.5a-d) in the Ganga, Mahanadi, Krishna and the Godavari estuaries display their conservative mixing. The linearity of all the data points which fall on the mixing line suggests that there is no addition from any other end member or removal of Sr in these mixing zones within analytical uncertainties. The calculated average precision based on replicate analysis, for the Sr concentration measurements, is found to be 0.75%. This precision makes difficult to distinguish addition or removal of Sr within ~1% and hence based only on Sr concentration, it becomes difficult to conclude Sr input from any other additional source in the studied estuaries. In contrast, the average precision of ⁸⁷Sr/⁸⁶Sr measurement is found to be 0.0011% (11 ppm; Table 4.2), which allows using ⁸⁷Sr/⁸⁶Sr variations as a more sensitive tracer to examine the mixing behavior of dissolved Sr in estuaries and any other source input. The records indicate 0.0020% variability, which is much higher than measured precision and hence can be used to look for additional source input.



Fig. 4.6: The plots (a-d) show the variations of dissolved 87 Sr/ 86 Sr with 1/Sr (kg μ mol⁻¹) in the (a) Ganga, (b) Mahanadi, (c) Krishna and (d) the Godavari estuary. The black line is the theoretical mixing line (TML) of two end members which are river and seawater. Most of the data points lie away from the TML suggesting non-conservative behavior of 87 Sr/ 86 Sr in these estuaries.

Mixing plot of 87 Sr/ 86 Sr vs. 1/Sr in all the estuaries indicate non-conservative nature of Sr in these estuaries (Fig. 4.6). Many of the data points deviate from the linear conservative mixing lines defined by the river and sea water end members. As indicated in Fig. 4.6, deviations in measured 87 Sr/ 86 Sr from the theoretical mixing line (TML) (> 20 ppm) possibly arise due to the supply of Sr from the additional source(s). Thus, the Sr isotope composition in estuarine waters may act as a better proxy to investigate the behavior of Sr as compared to Sr concentration and hence a mixing relationship of 87 Sr/ 86 Sr with 1/Sr is discussed in the following paragraph.

The binary relationship of 87 Sr/ 86 Sr over 1/Sr (kg µmol⁻¹), for the Ganga, Mahanadi, Krishna and the Godavari estuaries along with the TML's between the two end members are shown in Fig. 4.6a-d. Since Sr has longer residence time (3-5 Ma; Brass, 1976; Burke et al., 1982; Elderfield, 1986; Hodell et al., 1990) and no records are available of Sr in the BoB, we assume Sr concentration and 87 Sr/ 86 Sr ratio of other ocean to represent the BoB values that are 91.3 µmol kg⁻¹ and 0.7092, respectively (Palmer and Edmond, 1989; de Villiers, 1999). Fig. 4.6ad, clearly show that majority of the data points deviate from the TML beyond the analytical uncertainties i.e. clearly distinguishable by the measurements. Hence, the non-conservative nature of 87 Sr/ 86 Sr has been observed in all these estuaries. The observed departure of Sr isotope ratios in these estuarine waters from the predictable mixing line suggests the supply of radiogenic Sr from additional source in addition to the river and seawaters. Those additional sources could be SGD and/or the process of desorption/exchange from particles and/or sediments in the estuaries. Sr concentration and its isotope composition measured in the particulates rule out the possibility of being an addition source and hence SGD is the only candidate for the additional source of ⁸⁷Sr/⁸⁶Sr to these estuaries. The contribution to Sr concentration in these estuaries due to SGD is observed to be negligible with respect to the total concentration; however, it is significant in the distribution of ⁸⁷Sr. This may be because of the fact that the SGD is possibly a mixture of fresh groundwater and re-circulated seawater (Moore, 2010). Their mixing proportions can be decided by the hydraulic gradient in adjacent aquifers

and tidal conditions (Fig. 4.7). The similar studies in estuaries of the South China Sea, Narmada, and Tapi estuaries also reported the non-conservative behavior of Sr isotope in them (Wang et al., 2001; Xu and Marcantonio, 2004, 2007; Lin et al., 2010; Rahaman and Singh, 2012).



Fig. 4.7: Schematic of submarine groundwater discharge into coastal regions, modified after Burnett et al. (2006), and Rahaman and Singh, (2012).

4.3.1.3 Characterizing SGD and estimate of SGD fluxes in estuaries using inverse modeling

SGD flux has been quantified in this study using the inversion of salinity, Sr and ⁸⁷Sr/⁸⁶Sr mass balance equations followed by Rahaman and Singh (2012). In this method, it has been assumed that seawater, riverwater and SGD are the three possible sources, which control the composition of above mentioned parameters in estuarine waters. Inverse method has been used to assign the sources of solute budget to river water and to calculate the best values of the end members (Negrel et al., 1993; Gaillardet et al., 1999; Tripathy and Singh, 2010). The mass balance equations used in this study include the budget of salinity, Sr concentration and radiogenic Sr isotope composition in the estuary and fractional contribution from the three sources/end members. These equations are as follows,

where, i = 1-3 represents the possible sources, i.e. fresh river water, sea water and SGD; the subscript 'm' represents the measured values in each station and f_i is the fraction of water contributed to the estuary from source i.

It has been imagined that the data set is a quasi-linear combination of the variables and the measured set follows a log-normal probability distribution. The equations were solved using quasi-Newton method (Tarantola, 2005) where, minimization of misfit in the matrices was used to find the most probable set of variables and their uncertainties. The best solution or the *a posteriori* set with propagated errors was obtained based on a set of *a priori* values for all parameters from the inverse model.

The *a priory* value for the Ganga estuary, has been used from the earlier reported Sr concentrations and ⁸⁷Sr/⁸⁶Sr of groundwaters near estuary by Basu et al. (2001). In the case of Godavari estuary, *a priory* value of groundwater was taken as that of Sabari River water. However, *a priori* value of Sr and ⁸⁷Sr/⁸⁶Sr for the SGD entering into the Krishna estuary has been assumed as same as the value measured at zero salinity in the estuary due to the lack of Sr and ⁸⁷Sr/⁸⁶Sr data in the groundwater in the Krishna catchment. The calculated values of Sr concentration, ⁸⁷Sr/⁸⁶Sr and salinity of the SGD contributing to these estuaries give the best fit for the corresponding measured parameters.

Component	Salinity	Sr, µmol kg ⁻¹	⁸⁷ Sr/ ⁸⁶ Sr	€ _{Sr}
Ganga Estuary				
River water	0.001 ± 0.001	0.885 ± 0.1	0.731320	312
Seawater	35 ± 0.2	91.30 ± 2.0	0.7092	0
SGD (a priori)	0.1 ± 0.1	4.48 ± 0.5	0.724447	215
Krishna Estuary				
River water	0.001 ± 0.001	3.09 ± 0.1	0.713915	66
Seawater	35 ± 0.2	91.30 ± 2.00	0.7092	0
SGD (a priori)	0.1 ± 0.1	14.76 ± 0.5	0.713915	66
Godavari Estuary				
River water	0.001 ± 0.001	1.26 ± 0.1	0.714524	75
Seawater	35 ± 0.2	91.30 ± 2.00	0.7092	0
SGD (a priori)	0.1 ± 0.1	0.837 ± 0.5	0.718242	128

 Table 4.6: a priori data of Salinity, Sr and ⁸⁷Sr/⁸⁶Sr in river waters, seawater and

 SGD end member

Table 4.7: *a posteriori* values of SGD contributing salinity, Sr and ⁸⁷Sr/⁸⁶Sr to the Ganga, Krishna and the Godavari estuaries

Component	Salinity	Sr, µmol kg ⁻¹	⁸⁷ Sr/ ⁸⁶ Sr	٤ _{Sr}
Ganga-SGD	0.086 ± 0.082	3.78 ± 0.40	0.724446 ± 0.000002	81.8
Krishna-SGD	$4.43 \ \pm 0.082$	14.4 ± 0.40	0.713914 ± 0.000002	66.5
Godavari-SGD	0.10 ± 0.09	1.07 ± 0.10	0.718242 ± 0.000002	44.9

Salinity, Sr concentrations and ⁸⁷Sr/⁸⁶Sr of two of the three end members, river water and seawater are known (Table 4.6). As discussed in the previous section 4.3.1.2, the ⁸⁷Sr/⁸⁶Sr and Sr concentration of seawater end member is taken as 0.7092 ± 0.000010 and $91.3 \pm 2.0 \mu mol kg^{-1}$, respectively, reported for the open ocean waters (Palmer and Edmond, 1989; de Villiers, 1999) at salinity 35 (Table 4.6). The Krishna and the Godavari River end members are based on the measured values of samples collected during monsoon, 2013. In the case of Ganga estuary, river water end member is taken as 0.73132 (Chatterjee, 2013) for the third end member (SGD), there is no Sr data available, therefore *a priori* value for this end member was assumed to be the same as that measured in one of the nearby groundwaters.

The variations in the values of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios for the different end members are an order of magnitude lower as compared to the salinity and Sr concentrations used in the model. Therefore, to increase the model sensitivity to radiogenic Sr isotope composition, ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ values have been expressed as ϵ_{Sr} and defined as,

where, R is 87 Sr/ 86 Sr ratio, the subscripts 'rw' and 'sw' represent river water and seawater.

In this study, the calculations of SGD and Sr flux through SGD have been made for the Ganga, Krishna and the Godavari estuarine water samples. The model calculation go along with a posteriori values for the salinity, Sr concentration and ⁸⁷Sr/⁸⁶Sr ratios of SGD end member (Table 4.7; Fig. 4.8) and fraction of water supplied from the three end members to the estuary samples (Table 4.8). The calculated Sr concentration and ⁸⁷Sr/⁸⁶Sr of the SGD end member using inverse model are 3.78 ± 0.40 , 14.43 ± 0.40 , 1.07 ± 0.10 µmol kg⁻¹ and 0.724446, 0.713914 and 0.718242 with the salinity of 0.086, 4.43 and 0.10 for the Ganga, Krishna and the Godavari estuaries, (Table 4.7; Fig. 4.8) respectively. Due to less number of samples, we couldn't apply inverse modeling for the Mahanadi estuarine samples. The inferred salinity of the SGD signifies that it is recycled seawater. Waters from these estuaries penetrated the local aquifer during high tide and returned to the estuary during low tide (Sinha et al., 2010). In this cycling process, the estuary water exchanged its Sr pool with the sediments/aquifer solids in such a way that it makes the ⁸⁷Sr/⁸⁶Sr of the SGD more or less radiogenic without measurable changes in its Sr budget. The Ganga, Krishna and the Godavari Rivers have more radiogenic Sr compositions in their sediments as compared to seawater/estuary waters reflecting their respective lithology. Consequently, exchange of Sr isotopes between these sediments and estuary waters will result in more radiogenic ⁸⁷Sr/⁸⁶Sr in the SGD.



Fig. 4.8: Plots of ⁸⁷Sr/⁸⁶Sr vs. 1/Sr in the Ganga, Krishna and the Godavari estuaries (a-c). The data points plot with respect to the TML during monsoon, 2013. The departure of the data points from the TML is explained in terms of three end member, river water, seawater and submarine groundwater mixing. The Sr concentration and ⁸⁷Sr/⁸⁶Sr of the SGD end members estimated based on the inverse model is also plotted. RW, SW and GW represent riverwater, seawater and submarine groundwaters respectively.

Furthermore, ⁸⁷Sr/⁸⁶Sr of the SGD can be modified from the decay of ⁸⁷Rb to the ⁸⁷Sr during weathering (Blum and Erel, 1997; Colin et al., 1999) from aquifer sediments.

There is a wide range of SGD contribution, at various salinities, from ~ 1 to 16%, 1 to 7% and 12 to 50% (Table 4.8; Fig. 4.9) to the water budget of the Ganga, Krishna and the Godavari estuaries respectively. The uncertainties associated with the best fit estimates of the inverse model parameters are listed in Table 4.7. The contribution of SGD to the water flux of the eastern estuaries is calculated using the equation:

where, f_{ave} is the average SGD to river water ratio measured in the estuary and Q is the discharge, the subscripts 'SG' and 'riv' represent submarine groundwater and river water respectively. The Ganga and the Godavari estuaries showed large variations in their SGD. This variability might be because of variability in the river water flux. However, SGD of the Krishna estuary show ~20% of the river water flux. The average water discharge of the Hooghly, Krishna and the Godavari Rivers were 1650, 2213 and 3505 m³ s⁻¹ respectively (Subramanian, 1979; Rahaman and Singh, 2012; Rao and Sarma, 2013; Rengarajan and Sarma, 2015). This yielded annual SGD flux of the Hooghly, Krishna and the Godavari estuaries around ~270, 155 and 1735 m³ s⁻¹, respectively. The extrapolated SGD for the combined Ganga-Brahmaputra estuary is 5550 m³ s⁻¹ (calculated using water discharge of the G-B River, 33900 m³ s⁻¹; Basu et al., 2001; Singh et al., 2008 and SGD % of the Hooghly estimated in this study). The combined SGD from the Ganga-Brahmaputra, Krishna and the Godavari estuaries is ~2-10% of the global SGD (75-350 \times 10³ m³ s⁻¹), (Table 4.9; Fig. 4.10a; Zekster and Loaiciga, 1993; Beck et al., 2013). The estimated SGD flux of the G-B estuary, $(\sim 5550 \text{ m}^3 \text{ s}^{-1})$ in the monsoon period is marginally lower compared to the reported values for the combined G-B estuary (6350 $\text{m}^3 \text{ s}^{-1}$) in dry period by Basu et al. (2001). Generally, SGD increases during monsoon due to increase in water table. The discrepancy observed in SGD fluxes in the G-B could be due to different methodologies followed in the two studies. Rengarajan and Sarma, (2015) has calculated the typical SGD flux from the Godavari estuary during the non-monsoon period, by using 226 Ra and 228 Ra; ~40 m³ s⁻¹ which is significantly lower compared to the SGD (1735 m³ s⁻¹) estimated in the present study. The high SGD flow rates in the Godavari compared to earlier study (Rengarajan and Sarma, 2015) could be due to the difference in the sampling season. This study has been carried out during monsoon compared to post-monsoon season sampling of Rengarajan and Sarma (2015). As discussed earlier, SGD is always higher during monsoon period due to increased water table.

4.3.1.4 SGD flux of Sr from the East Indian estuaries to the Bay of Bengal

The Sr flux through SGD, based on the Sr concentration and isotope data (Table. 4.9) and SGD as estimated in the previous section, from the Hooghly, Krishna and the Godavari estuaries have been calculated to be (32.2, 59.4 and 58.7) \times 10⁶ mol y⁻¹ with ⁸⁷Sr/⁸⁶Sr of 0.724446, 0.713914 and 0.718242, respectively. The Sr flux through SGD based on the G-B water discharge is $660 \times$ 10⁶ mol y⁻¹. The respective annual Sr fluxes of the Krishna and the Godavari Rivers are 216×10^6 and 140×10^6 moles based on the water flux of 2213 and $3505 \text{ m}^3 \text{ s}^{-1}$ for both the rivers with Sr concentrations of 3.09 and 1.26 µmol kg⁻¹ (Table 4.2). Sr fluxes through SGD of the Krishna and the Godavari basins are ~30 and 40% of their riverine supply and that in the G-B estuary (660×10^6 mol y⁻¹) is ~25% of its riverine Sr. Sr fluxes of G-B SGD is marginally lower compared to the estimates of Basu et al. (2001). The Combined Sr flux through SGD by three river systems to the BoB contributes about 3-11% to the global Sr flux through SGD ((0.7-2.8) \times 10¹⁰ mol y⁻¹), (Fig. 4.10b; Zekster and Loaiciga, 1993; Beck et al., 2013). The recycling process causing the alteration in the isotope composition of Sr through exchange between aquifer solids and seawater makes it more radiogenic, i.e. enriched in ⁸⁷Sr with respect to the seawater. As a result, the SGD supply an additional amount of ⁸⁷Sr to the East Indian estuaries. It can be estimated globally, based on Sr flux and difference in the ⁸⁷Sr/⁸⁶Sr of SGD and seawater. The ⁸⁷Sr supply from SGD needs to be included in the global Sr isotope budget of seawater, however, its impact on both regional and global scale



is difficult to assess currently due to lack of data from various estuaries and coastal regions.

Fig. 4.9: Ternary plot shows the contributions of seawater, river water and SGD near the Ganga, Krishna and the Godavari estuaries.

Sample	Loca	ition	Salinity	Contribut	ion of wate	r flux (%)
	Latitude	Longitude		RW	SW	SGD
Ganga estuary ((24th July, 201					
Hooghly-13/02	22°12'40.7"	88°3'55.4"	0.3	83.4	0.8	15.8
Hooghly-13/01	22°12'26.3"	88°4'1.20"	0.4	82.5	1.1	16.4
SM-24-13/01	22°01.140'	88°04.965'	3.8	75.6	10.8	13.6
SM-24-13/02	21°58.930'	88°02.706'	4.8	73.9	13.6	12.5
SM-24-13/03	21°56.327'	88°01.293'	6.5	67.2	18.5	14.3
SM-24-13/04	21°54.630'	88°00.585'	7.8	65.5	22.2	12.3
SM-24-13/05	21°52.940'	87°59.747'	9.7	60.5	27.6	11.9
SM-24-13/06	21°49.980'	87°58.685'	11.3	55.3	32.2	12.5
SM-24-13/07	21°47.497'	87°57.865'	13.8	50.6	39.3	10.1

Table 4.8: Contribution of seawater, river water and SGD along the salinity

 gradient in the Ganga, Krishna and the Godavari estuaries

SM-24-13/08	21°46.859'	87°57.920'	18.6	36.0	53.0	11.0
SM-24-13/09	21°45.244'	87°58.414'	21.3	31.2	60.7	8.1
SM-24-13/10	21°37.870'	88°01.967'	23.3	31.0	66.5	2.6
SM-24-13/11	21°18.677'	88°11.687'	19.1	44.8	54.5	0.7
SM-24-13/12	20°35.993'	87°52.428'	29.4	15.7	83.9	0.4
Krishna estuary	y (24th August	t, 2013)				
KR-13/01	16°01'51.0"	80°52'28.5"	0.0	98.8	0.1	1.0
KR-13/02	15°50'24.8"	80°52'04.0"	0.5	94.9	0.9	4.2
KR-13/03	15°46'09.5"	80°50'29.3"	1.9	89.9	4.7	5.4
KR-13/04	15°45'37.8"	80°50'14.0"	2.7	87.7	7.0	5.2
KR-13/05	15°45'20.2"	80°50'08.8"	4.0	84.2	10.7	5.1
KR-13/06	15°45'19.6"	80°50'06.7"	5.1	80.5	13.8	5.8
KR-13/07	15°44'47.1"	80°49'56.5"	6.9	75.6	18.9	5.5
KR-13/11	15°43'48.8"	80°49'48.8"	10.3	66.9	28.8	4.3
KR-13/10	15°43'23.3"	80°49'50.9"	14.6	52.1	40.6	7.3
KR-13/09	15°43'27.3"	80°49'50.0"	18.1	44.5	50.9	4.5
KR-13/08	15°43'33.0"	80°49'49.9"	30.2	13.1	85.8	1.0
Godavari estua	ry (2nd Septer	nber, 2013)				
GDV-13/18	16°43'17.4"	82°12'33.5"	0.0	87.8	0.1	12.1
GDV-13/19	16°46'35.4"	82°21'36.7"	1.6	68.7	4.5	26.8
GDV-13/20	16°46'50.2"	82°21'46.8"	2.8	48.1	7.8	44.1
GDV-13/21	16°47'20.8"	82°22'45.1"	5.1	41.1	14.4	44.5
GDV-13/22	16°47'23.3"	82°22'56.3"	6.4	37.8	18.1	44.1
GDV-13/23	16°47'16.4"	82°23'50.6"	10.0	36.9	28.3	34.7
GDV-13/24	16°47'18.2"	82°24'10.8"	12.2	15.9	34.6	49.6
GDV-13/25	16°47'10.8"	82°24'58.3"	15.0	14.1	42.6	43.3

Table 4.9: The SGD flux and Sr flux through SGD along with their errors (error propagation)

	SGD flux	± SGD flux	Sr flux	± Sr flux
Estuary	$10^3 \text{m}^3 \text{s}^{-1}$	$10^3 \text{m}^3 \text{s}^{-1}$	10 ⁸ mol y ⁻¹	10 ⁸ mol y ⁻¹
Hooghly	1.22	0.04	0.322	0.05
Ganga	1.97	0.30	2.348	0.36
G-B	5.55	0.85	6.610	1.02
Krishna	0.16	0.01	0.594	0.04
Godavari	1.74	0.45	0.587	0.15
Global #	75-350	-	70-280	-

#: Zekster and Loaiciga, 1993; Beck et al., 2013.



Fig. 4.10: The plots show (a) the SGD in the East Indian estuaries with respect to the global SGD and (b) the Sr flux through SGD in the East Indian estuaries with respect to the global Sr via SGD.

4.3.2 Elemental, Sr, Nd and 87 Sr/ 86 Sr, ε_{Nd} in the estuary sediments

Sediments have been collected along with waters from the Ganga, Krishna and the Godavari estuaries during monsoon, 2013. In the present season, the SPM in the Ganga estuary exists in the range of 2-36 tons km⁻² y⁻¹ which is on an average comparable to the reported values from the Ganga in the Himalaya (Bhagirathi, Alaknanda and Yamuna) in the range of 10-25 tons km⁻² yr⁻¹ (Krishnaswami and Singh, 2005) debouched into the BoB. Major elemental compositions, concentration of Sr, Nd and ⁸⁷Sr/⁸⁶Sr, ε_{Nd} have been measured in the silicate fraction of the sediments of these estuaries (Table. 4.5). Al₂O₃-CaO+Na₂O-K₂O (A-CN-K) ternary diagram (Fig. 4.11) shows the weathering trends for the sediments in the Ganga, Krishna and the Godavari estuarine samples.



Fig. 4.11: Al₂O₃-CaO+Na₂O-K₂O (A-CN-K) ternary diagram shows the weathering trends for the sediments in the Ganga (red), Krishna (blue) and the Godavari (GDV; green) estuarine samples.

The analyzed Sr and Nd isotope compositions in the SPM from the Ganga estuarine vary from 0.757737 to 0.766794 and -15-3 to -18.1, respectively. In the Godavari estuarine, Sr and Nd isotope compositions sediment vary with a wide range of 0.731446 to 0.745686 and -17.4 to -27.1, and In the Krishna estuary, which exists as 0.739268 and -23.5 respectively. The isotopic compositions of various other end members which can contribute to the Ganga, Krishna and the Godavari sediments are plotted (Fig. 4.12). The isotopic composition of SPM from the Ganga is deduced in terms of a binary mixing, Higher Himalaya (HH) and Lesser Himalaya (LH). The binary mixing plot (Fig. 4.12) suggesting that, the HH sediments erodes and contributing more than the other sources like the Vindhyan and the Godavari are almost similarly influenced through the Deccan basalts and Cratons.



Fig. 4.12: The mixing plot of Sr-Nd isotopes of SPM from the Gang, Krishna and the Godavari estuary. The isotopic composition of SPM from the Ganga is deduced in terms of a binary mixing, HH and LH. The isotopic compositions of various other end members which can contribute to the Ganga, Krishna and the Godavari sediments are also shown.

4.3.3 Behavior of the dissolved REEs and ε_{Nd} in mixing zone

Focus of this section is on the behavior of concentrations of dissolved Mn and REEs and Nd isotope composition in the Ganga, Mahanadi, Krishna and the Godavari estuary. We also examined the behavior of Nd concentrations and its isotope ratios in particulates from these estuaries. Except the Godavari, concentration of the dissolved Mn and REEs displays bi-modal distributions in the mixing zones of the eastern estuaries. Near the low salinity zone, a significant removal of dissolved Mn and REE has been observed in three estuaries, the Ganga, the Mahanadi and the Krishna (Fig. 4.2 and 4.4). This removal of dissolved Mn and REE could be due to salt – induced coagulation of river colloids (Goldstein and Jacobsen, 1987; Elderfield et al., 1990; Sholkovitz, 1993; Kim and Kim, 2014; Rousseau et al., 2015). The removal of dissolved Mn in the Ganga, Mahanadi and the Krishna estuary waters is 28, 67 and 50%, respectively. Such removal of dissolved REEs and Fe also has been observed in the Great Whale, Amazon, Fly, Gulf of Papua and Sepik Riverine estuaries (Goldstein and Jacobsen, 1988b, c; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000; Rousseau et al., 2015). A moderate to a high removal of REEs (10-80%) is observed in low salinity zones of these estuaries. This removal is lower compared to that reported for REEs (56-97%) in the Great Whale, Amazon, Fly, Gulf of Papua, Sepik, Mullica and the Connecticut estuaries (Goldstein and Jacobsen, 1988b, c; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000; Rousseau et al., 2015). For instance, the removal of dissolved Nd in the Ganga, Mahanadi and the Krishna estuary is 58, 64 and 20%, respectively (Fig. 4.13) which is marginally lower compared to the Great Whale, Amazon, Fly, Sepik, Mullica and the Connecticut estuaries, 60, 95, 87, 81, 81 and 56%, respectively (Goldstein and Jacobsen, 1988b, c; Elderfield et al., 1990; Sholkovitz, 1993; Sholkovitz and Szymczak, 2000; Rousseau et al., 2015). The results clearly show that, the rivers with the high Nd concentration and low pH values are effective to the excess removal of trace elements in low salinity zones (e.g. Mahanadi estuary) compared to the rivers with the low Nd with high pH (e.g. Krishna estuary). In the Godavari estuary, high pH with the low Nd concentration at the river end member was

observed, which may be the basis for no removal of trace elements (e.g. REEs and Mn) in this estuary. The similar behavior has been observed in Gironde estuary by Martin et al. (1976). The minor depletion in the concentration of REEs observed in the present study might be because of low biological activity in these estuaries. The high biological activities have been found to remove the trace metals from the water column by coagulation of river colloids (Sholkovitz, 1993). The estimated annual dissolved Nd fluxes of the Ganga, Mahanadi, Krishna and the Godavari River into their estuaries are ~6.5, 1.6, 0.2 and 1.1 Mg, respectively (based on a Nd_{riv} in freshwaters and the annual discharges of the Ganga, Mahanadi, Krishna and the Godavari River; Trivedi et al., 1995; Gaillardet et al., 1999; Galy et al., 1999; Chatterjee, 2013). As has been observed earlier, part of the trace elements, REEs supplied by rivers is removed through the salt-induced coagulation of river colloids in the low salinity zone of these estuaries except in the Godavari estuary. No such removal is observed in the concentration of the dissolved Nd and other trace elements in the Godavari estuary. After initial removal, a moderate to a rapid release of trace elements in these estuaries are observed in the mid and high salinity zones.



Fig. 4.13: The riverine concentration normalized Nd patterns in the East Indian Estuaries.

Rapid release of dissolved REEs and Mn has been observed in the mid and high salinity zones of all the estuaries (Fig. 4.13). In the Godavari estuary, continuous enrichment has been observed in the concentrations of dissolved REEs and Mn along with the salinity (from S = 0 to 15). This release of trace elements in these estuaries could be due to desorption of REEs coated on SPMs along with Fe-Mn oxy-hydroxides and/or dissolution of REEs containing SPM solid phase, leaching of trace metals from nearby land masses through submarine groundwater discharge (SGD) (Hoyle et al., 1984; Goldstein and Jacobsen, 1988b, c; Elderfield et al., 1990; Sholkovitz and Szymczak, 2000; Kim and Kim, 2014; Rickli et al., 2014; Rousseau et al., 2015). Most probable explanation for the rapid release of REEs in the mid/high salinities region is their desorption from Fe-Mn oxyhydroxides in the low oxygen zone as the abrupt release of dissolved REEs in the mid and high salinities in the Ganga estuary is associated with decrease in oxygen content and increase in dissolved Mn (Fig. 4.14). Most probably it happens near the water-sediment interface where micro-environment of redox/suboxic conditions are getting created leading to the dissolution of Fe-Mn oxy-hydroxide soluble in reducing condition) releasing dissolved REEs to the water (Fig. 4.14). Highly turbulent water in these salinity zones during monsoon churns the sediment and mixes the REEs enriched water from the sediment-water interface to the entire water column. This is also reflected by the high concentration (as high as $\sim 2 \text{ g L}^{-1}$) of particulate matters in this zone. Further, to ascertain the nature of release of REEs in the water column, Nd and its isotope composition have also been analyzed in particulates from the Ganga, Krishna and the Godavari estuaries (Table 4.5). The SPM concentration varies from 0.1 to 1.7 g L^{-1} in the Ganga estuary. The SPM is quite low at the beginning of the estuary, near zero salinity, enhances at mid salinities (S = 3.8-9.7) and gets depleted to a minimum in the higher salinities (S \geq 10). It signifies that, near the mid salinity zone re-suspension process of sediments increase its concentration. In the Ganga estuary, ε_{Nd} of the dissolved phase always more radiogenic compared to particulates by about 3.5 ε units (Fig. 4.15a) similar to that observed in the Amazon estuary (Rousseau et al., 2015), whereas, in the Krishna and Godavari estuaries this difference is high (6ϵ), indicating isotope fraction due to preferential chemical weathering of minerals and/or different sources of dissolved/particulate Nd (Fig. 4.15c, d). In these estuaries, the particulate Nd concentration and their ε_{Nd} values vary from 14 to 16.4 µg g⁻¹ and -18.5 to -15.3, respectively. In the Ganga estuary, near the salinity ~7, ε_{Nd} in both the dissolved and particulates shift towards less radiogenic values and the particulate ε_{Nd} at this point is similar to its value near the freshwaters (Fig. 4.15a). All the above observation in the present study conclude that the enrichment in the concentration of dissolved Mn and REEs in the mid and high salinity locations are because of desorption and/or dissolution of the Fe-Mn hydroxides.



Fig. 4.14: The dissolved Oxygen (DO, red diamonds with dashed line), dissolved Nd (green star with a continuous line) and dissolved Mn (blue squares with dashed line) vs. salinity in the Ganga estuary.

To quantify the fraction of Nd that has been released from the SPM in the mid/high salinity regions, we applied a couple of mass balance equations as follows:

$$\varepsilon_{Nd_m} \times Nd_m = \sum_{i=1}^n \varepsilon_{Nd} \times Nd_i \times f_i$$
4.8

where, f indicates the fraction of possible sources (freshwater, seawater and SPM), subscript 'm' represents measured parameter and the three dissolved Nd fractions have corresponding $\varepsilon_{Nd(riv)}$, $\varepsilon_{Nd(SPM)}$ and $\varepsilon_{Nd(sea)}$. The respective concentration of Nd and $\varepsilon_{Nd(riv)}$ in the water (at S = 0) and particulate materials of the Ganga, Mahanadi, Krishna and the Godavari River end members have been listed in Table 4.5 and 4.5 (present study). Here, the seawater (BoB) end-member of Nd concentration and ε_{Nd} assumed as 34 pmol kg⁻¹ and -15.0 (Singh et al., 2012). The major fraction of dissolved Nd released from SPM in the Ganga and the Godavari estuaries are at salinities 7.8 and 15.0, respectively (Table 4.4, Fig. 4.15a, d). A significant fraction of release of Nd from SPMs is also observed at other salinities in the Ganga (such as SM-24-13/12 in the Ganga) and the Godavari estuary. The released Nd flux from the particulates of the Mahanadi, and the Krishna estuaries could not be estimated due to lack of SPM data. The annual dissolved Nd fluxes in the Ganga (considering the entire Ganga), Mahanadi, Krishna and the Godavari, released from their SPM are 250, 0.54, 1.25 and 6.75 Mg respectively, are significant in terms of missing Nd (11000 to 5500 Mg) to its global budget (Arsouze et al., 2009; Rempfer et al., 2011; Tachikawa et al., 2003). Nd_{SPM} flux from SPM in the Ganga and the Godavari estuaries (based on Nd_{SPM} of Ganga and Godavari are 27 and 8.5 μ g g⁻¹ and their discharge of 4.93 x 10^{14} (entire Ganga) and 1.1 x 10^{14} L y⁻¹; Gaillardet et al., 1999; Singh et al., 2008) are 13500 and 1445 Mg y⁻¹, respectively. Out of these particulate Nd, 1.85 and 0.47% are getting released in the Ganga and the Godavari estuary, respectively. The combined Nd release from SPM in the Ganga and the Godavari estuaries is approximately 45 times higher than their riverine dissolved Nd flux to the BoB. The total dissolved Nd flux released from SPM of the Ganga and the Godavari into the BoB (~260 Mg) is 1.4 times higher compared such released Nd flux (186 Mg) from SPM to the Atlantic Ocean. The total dissolved Nd released from SPM of the Ganga and the Godavari estuary contributes varies with a range of ~2 to 5% to the missing Nd source flux in global budgets (5500-11000Mg; Rousseau et al., 2015). It signifies these estuaries are the potential sources to the missing Nd source budget in the World Ocean.



Fig. 4.15: The distribution patterns in the concentration of the dissolved Nd and dissolved and particulate ε_{Nd} over salinity in the East Indian estuaries. The inset in the plot (d) shows the legend.

In all the estuaries, PAAS normalized dissolved REEs patterns show coherent nature, encouraging their application as proxy of their sources. The dissolved Nd concentration and its isotope composition in the river water end members show a great variation, signifying large variation in their basin lithology. Fractionations occur during both the removal and re-release of REEs in the surface waters, which have been observed in the patterns of PAAS normalized REEs (Fig. 4.16a-d). Negative Ce anomaly is observed in waters of the Mahanadi, Godavari and

Krishna estuaries. However, no such Ce anomaly has been observed in the Ganga estuary in the minimum DO zones, which might be because of more solubility of Ce in suboxic conditions. A moderate enrichment of HREE is observed in all the estuaries. Enrichment in all the REEs at mid to high salinity regions in all the estuaries is evident in these PAAS normalized patterns very clearly.





Fig. 4.16 (a-d): The plots show that the PAAS normalized REEs fractionations between LREE-MREE-HREEs of the East Indian Estuaries, shows the coherent nature.

4.4 Implications

The concentrations of dissolved trace elements and ε_{Nd} in the estuaries are regulated by the mixing between river and seawater and sediment-water interactions, their drainage basin lithology, hydrography and morphology of the estuaries. Two distinct processes are operational on dissolved Mn and REEs in the East Indian estuaries. A moderate to an extreme removal of dissolved Mn and REEs near low salinity zone followed by their abrupt and extensive release in mid and high salinity regions are observed. The annual flux of released Nd from the SPMs in the Ganga and the Godavari estuaries is 250 and 6.75 Mg, respectively. Together they contribute ~2 to 5% of the global ocean missing Nd (5500 - 11000 Mg) sources. Such sources can contribute to the other redox-sensitive trace elements (e.g., Osmium, Molybdenum and Uranium). In anoxic conditions, Fe-Mn oxy-hydroxides act as a source of dissolved Uranium (U) and Molybdenum (Mo) during their reductive dissolution (Shimmield and Price, 1986; Calvert and Pedersen, 1993; Audry et al., 2006, 2007).

4.5 Summary and conclusions

Efforts were made to quantify the annual dissolved Sr budget and its isotopic composition (87Sr/86Sr) in the Ganga, Godavari, Mahanadi and the Krishna estuaries of east India. The results show significant differences in Sr and its ⁸⁷Sr/⁸⁶Sr among the river waters which can be understood in terms of their drainage basin lithology. The relationship between the concentration of Sr and salinity clearly show "near perfect" conservative mixing between riverwater and seawater indicating no additional source. However, the mixing relationship of ⁸⁷Sr/⁸⁶Sr and 1/Sr clearly indicates the non-conservative behavior of Sr isotopes in these estuaries. The deviation of 87 Sr/ 86 Sr from the binary mixing is explained in terms of supply of Sr from SGD with isotopically distinct ⁸⁷Sr/⁸⁶Sr. An inverse model based on concentration of Sr, ⁸⁷Sr/⁸⁶Sr ratio and salinity confirms SGD as an additional source, which discharges water flux of about 15, 7 and 50% of the riverine water discharges in the G-B, Krishna and the Godavari estuary, respectively. This indicates that, the SGD in these estuaries primarily is recycled water, which exchanges Sr with the aquifer sediments becoming more radiogenic in Sr without changing its concentration of Sr. Thus, the SGD acts as a source of ⁸⁷Sr to the BoB. The average SGD flow rate during monsoon season in the G-B, Krishna and the Godavari estuaries are 5545 ± 845 , 155 ± 15 and 1735 ± 45 m³ s⁻¹ respectively. These SGD flow rates annually supplies (660, 59.4 and 58.7) $\times 10^{6}$ moles of Sr to the G-B, Krishna and the Godavari estuaries respectively and hence to the BoB. The overall annual Sr flux through the SGD from East Indian estuaries is 7.8×10^8 mole which is ~3-11% of the global annual SGD Sr flux $(0.7-2.8 \times 10^{10} \text{ mole})$ with annual seepage is $0.75 \times 10^4 \text{ m}^3 \text{ s}^{-1}$ is about 2-10% of the global annual SGD ((7.5-35) \times 10⁴ m³ s⁻¹). This study emphasizes the application of the concentration of Sr and its isotope composition to quantify the flux of submarine groundwater seepage and trace elements to the estuaries and ultimately to the oceans.

The hydrographical and morphological properties of the estuaries play a key role in removal and/or release of trace elements in the mixing zones. The estuarine sediments also act as considerable sources of dissolved TEIs to the estuaries and finally to the open ocean. Two distinct processes, removal of trace metals (e.g. REEs, Mn) at low salinity zone due to salt-induced coagulation of river colloids and their release in the mid and high salinity zones are operation in the East Indian estuaries. REEs and Mn are released in the mid/high salinity regions due to re-dissolution or desorption from Fe-Mn oxy-hydroxides coated on SPM. The fractionation in the concentration of REEs happens during both removal and release in the mixing zones. The fractionation in concentration of dissolved REEs leads to change their relative abundances in the oceanic REEs budget. In these estuaries, micro-suboxic zones operate as a principal controlling parameter of dissolved REE and Mn. Re-dissolution of Fe-Mn oxy-hydroxides act as an important source of dissolved trace elements (REEs, Fe-Mn, and lighter Mo etc.). The SPM dissolution and SGD also can contribute the excess amount of dissolved REEs in the mixing zones. The dissolution/desorption of/from particles in the east Indian estuaries are the potential sources of dissolved Nd, ~260 Mg per year from the Ganga and the Godavari estuaries, which could be very significant contribution to the missing Nd and similarly it could be important source of other trace elements to their global oceanic budgets.

Chapter 5

Lithology, Monsoon and Sea-Surface Current Control on Provenance, Dispersal and Deposition of Sediments over the Andaman Continental Shelf

5.1 Introduction

Rivers are the primary transporters of physically and/or chemically weathered continental materials to the ocean. They play a prominent role in the evolution of coastal and deep sea sediments. Terrigenous sediments eroded from the Himalayas, Myanmar, and Indo-Burman subcontinents are deposited to the Andaman Sea by rivers such as the Irrawaddy (Aveyarwaddy), the Salween (Thanlwin), the Sittang, the Kaladan and the Tanintharyi etc. The Irrawaddy is the third largest river in the world in terms of suspended sediment discharge and together with the Salween contributes ~550 million tons (MT) of sediment annually (Robinson et al., 2007). Intense monsoon causes higher runoff in the Irrawaddy Basin, which in turn enhances erosion in the catchment area. The sediments brought by the Irrawaddy and the Salween Rivers are deposited in the Northern and Eastern shelf of Andaman Sea with a width of more than 170 km. A significant amount of terrestrial organic matter brought by these rivers is deposited along with them influencing the long-term carbon cycle (France-Lanord and Derry, 1997; Bird et al., 2008; Ramaswamy et al., 2008). The sources of these sediments deposited on Northern and Eastern Andaman Shelf and the factors controlling the erosion of this large volume of sediments are poorly constrained due to complicated logistic and political reasons associated with their sampling. The seasonally reversing surface circulation controlled by the monsoon (Rodolfo, 1969; Ramaswamy et al., 2004; Rao et al., 2005) influences the dispersion and deposition of these sediments significantly. Influence of the Irrawaddy and the Salween Rivers on the sedimentary budget of the Eastern Bay of Bengal (BoB) is still a matter of debate, though they deliver huge amount of sediments into the Andaman Sea (Rao et al., 2005; Robinson et al., 2007). The sediments deposited in the Andaman Sea brought down by these river systems, preserve imprints of the erosion and weathering history of Himalayan and Burman Ranges (Colin et al., 1999). Detrital sediments are primarily the weathered products of continental rocks with a wide range of Sr and Nd isotope ratios. The distinct isotopic

compositions of these sediments can be used to track their provenance (Goldstein et al., 1984; Colin et al., 1999; Galy and France-Lanord, 2001; Singh and France-Lanord, 2002; Singh et al., 2008; Tripathy et al., 2011; Goswami et al., 2012). In the present study, the Sr and Nd isotopic composition and major elemental concentrations of silicate fractions of surface sediments of the Northern and Eastern Andaman Shelf are measured to track their provenances. Further, an effort has been made to evaluate the role of climate and tectonics in controlling the erosion in its catchment and to assess the impact of surface ocean circulation in controlling the dispersal and deposition of these sediments.

5.2 The abundances of major elements, Sr and Nd and Sr-Nd isotope compositions in the Andaman Shelf basin

A total of 110 surface sediment samples were collected from the Northern shelf of Andaman Sea region during the low river discharge period of April-May, 2002 onboard the 175th expedition of ORV Sagar Kanya (Fig. 5.1; Ramaswamy et al., 2008). The details of the sampling locations are listed earlier in chapter-2 (Table 2.4). The Northern and Eastern Andaman Shelf sediment samples analyzed in this study are dominated by silt and clay fractions (Rodolfo, 1969; Rao et al., 2005; Ramaswamy et al., 2008) with coarser sand dispersed at places. The concentrations of major elements such as Na, K, Ca, Mg, Al, Fe, Mn, and Ti measured in silicate fraction of the shelf and river sediments are reported in Table 5.1. The relative abundances of these elements in the shelf sediments were observed in an increasing order, Mn < Ti < Ca < Na < Mg < K < Fe < Al. This trend originates in large extent from the earth crust through weathering. The concentrations of major elements display a large variation (Table 5.1). Al is the most abundant in most of the samples followed by Fe. Al and Fe vary from 0.5 to 13.1 wt% and 0.5 to 6.1 wt%, respectively, which are within the typical range for rock forming minerals (Alagarsamy et al., 2010). A few sediment samples collected near the Mergui shelf along Southern Myanmar (Fig. 5.1) contain lower content of Al and other elements probably due to the dominance of quartz in them. Ca varies from 0.07 to 0.94 wt% in these de-carbonated samples. Al and Fe contents in Irrawaddy River sediment are high, 12 and 6 wt%, respectively whereas they are ~6 and 3 wt%, respectively in Salween River sediments. The concentrations and isotopic compositions of Sr and Nd of shelf and river sediments are presented in Table 5.1. The ranges of Sr and Nd concentrations are $10-162 \ \mu g \ g^{-1}$ and $2.4-38.6 \ \mu g \ g^{-1}$, respectively, and are generally lower or comparable to the values reported for Irrawaddy, Salween, and Ganga–Brahmaputra (G–B) River sediments (Colin et al., 1999; Singh et al., 2008).



Fig. 5.1: The lithology map of the drainages of the Irrawaddy, Salween and the Tanintharyi River basins falling in the Tibet, China, and the Myanmar, modified after (Awasthi et al., 2014; Chapman et al., 2015).

Table 5.1: Sample locations, major element compositions, concentrations and isotope compositions of Sr and Nd and Chemical Index of Alteration (CIA) in surface sediment samples from the Irrawaddy continental shelf, Northern Andaman Sea and the Irrawaddy and the Salween Rivers

Station	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	MnO	TiO ₂	[Sr]	⁸⁷ Sr / ⁸⁶ Sr	[Nd]	¹⁴³ Nd/ ¹⁴⁴ Nd	$\epsilon_{Nd}(0)$	CIA
No.				w	t %				$\mu g g^{-1}$		μg g ⁻¹	-		
SK-175/3	1.02	2.30	0.17	2.51	24.77	7.64	0.031	0.94	54	0.716734	19.3	0.512315	-6.3	88
SK-175/5	1.12	1.32	0.45	1.44	13.25	5.30	0.034	0.74	162	0.713101	19.6	0.512268	-7.2	82
SK-175/10	1.47	1.03	0.76	1.02	8.28	3.91	0.030	0.76	108	0.713014	18.5	0.512162	-9.3	72
SK-175/14	0.62	1.15	0.37	1.23	9.79	5.51	0.035	0.70	65	0.716388	18.5	0.512104	-10.4	82
SK-175/20	0.46	1.16	0.37	0.57	3.12	2.62	0.020	0.34	57	0.713403	7.3	0.512044	-11.6	61
SK-175/22	1.29	1.00	0.98	1.28	5.88	3.96	0.044	0.44	113	0.713586	10.9	0.512076	-11.0	64
SK-175/24	1.41	1.26	1.03	1.41	7.41	3.49	0.030	0.43	128	0.712245	4.5	0.512075	-11.0	67
SK-175/26	1.29	1.39	0.81	1.28	10.82	3.31	0.029	0.64	100	0.715966	17.9	0.512162	-9.3	76
SK-175/27	0.66	1.38	0.53	0.53	5.08	2.00	0.019	0.30	76	0.715593	2.4	0.512069	-11.1	66
SK-175/32	1.37	1.44	0.84	1.60	11.46	4.17	0.038	0.65	95	0.715572	18.7	0.512077	-10.9	76
SK-175/34	1.25	1.56	0.80	1.49	10.25	4.01	0.037	0.54	148	0.714846	14.1	0.512101	-10.5	74
SK-175/36	1.38	1.38	0.75	1.43	11.07	4.60	0.035	0.70	95	0.714517	18.1	0.512113	-10.2	76
SK-175/39	0.98	1.61	0.38	1.64	14.24	5.87	0.034	0.85	81	0.717919	22.2	0.512132	-9.9	83
SK-175/41	0.75	2.01	0.30	2.05	18.84	6.12	0.039	0.90	70	0.720995	20.6	0.512146	-9.6	86
SK-175/44	0.80	1.83	0.32	1.77	16.87	5.56	0.036	0.82	69	0.721241	23.7	0.512091	-10.7	85
SK-175/45	0.73	1.81	0.31	1.63	16.18	5.82	0.041	1.01	76	0.721578	23.7	0.512071	-11.1	85
SK-175/46	0.90	1.81	0.38	1.54	15.45	5.50	0.038	0.75	78	0.720775	22.7	0.512069	-11.1	83
SK-175/47	0.92	1.85	0.38	1.57	15.37	5.77	0.042	0.99	66	0.720946	38.6	0.512102	-10.4	83
SK-175/48	0.77	1.88	0.27	1.49		7.25	0.042	0.97	68	0.722994	27.5	0.512087	-10.8	
SK-175/49	0.87	1.95	0.32	1.65	16.70	6.07	0.049	0.86	72	0.722443	24.6	0.512053	-11.4	84
SK-175/50	0.71	1.56	0.29	1.25	11.87	6.02	0.040	0.82	71	0.723430	25.3	0.512078	-10.9	82
SK-175/51	0.75	1.59	0.30	1.30	12.76	6.28	0.052	0.83	70	0.723142	31.1	0.512079	-10.9	83

191 | Page

Station	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	MnO	TiO ₂	[Sr]	⁸⁷ Sr / ⁸⁶ Sr	[Nd]	¹⁴³ Nd/ ¹⁴⁴ Nd	$\epsilon_{Nd}(0)$	CIA
No.				w	t %				μg g ⁻¹	-	µg g ⁻¹	-		
SK-175/52	0.77	1.46	0.42	0.60	5.70	2.70	0.023	0.34	66	0.722788	13.0	0.511959	-13.2	68
SK-175/54	0.84	1.74	0.34	1.71	16.02	6.67	0.047	0.80	70	0.722522	22.5	0.512108	-10.3	85
SK-175/55	0.82	1.69	0.36	1.64	14.30	6.17	0.042	0.85	73	0.724791	28.7	0.512088	-10.7	83
SK-175/57	0.81	1.82	0.39	1.75	16.16	5.95	0.053	0.78	74	0.722000	24.9	0.512092	-10.6	84
SK-175/66	0.74	1.93	0.27	1.88	18.07	6.56	0.046	0.88	71	0.722268	24.9	0.512093	-10.6	86
SK-175/69	0.94	1.78	0.55	0.82	8.66	2.57	0.029	0.42	80	0.722260	22.4	0.511973	-13.0	73
SK-175/70	0.21	0.70	0.11	0.77	5.89	1.78	0.014	0.22	66	0.724474	10.8	0.512082	-10.8	85
SK-175/71	0.79	1.86	0.35	1.69	15.79	5.55	0.044	0.74	61	0.721855	23.2	0.512050	-11.5	84
SK-175/72	0.75	2.03	0.29	1.72	17.16	6.05	0.039	0.81	66	0.722437	27.7	0.512078	-10.9	85
SK-175/76	1.32	1.58	1.05	1.45	11.07	4.17	0.036	0.69	112	0.714620	20.0	0.512054	-11.4	74
SK-175/79	0.64	1.16	0.51	0.22	2.64	1.65	0.020	0.55	66	0.724030	17.8	0.511945	-13.5	53
SK-175/80	0.66	1.25	0.42	0.27	3.25	1.94	0.022	0.47	67	0.722759	9.0	0.511990	-12.6	58
SK-175/83	0.55	1.61	0.24	0.89	9.97	6.97	0.027	0.65	53	0.726911	17.0	0.511973	-13.0	81
SK-175/87	1.22	1.65	1.12	1.38	11.56	3.66	0.038	0.98	115	0.716841	22.8	0.512085	-10.8	74
SK-175/94	0.97	1.64	0.57	1.78	14.51	4.89	0.036	0.71	87	0.717886	17.2	0.512093	-10.6	82
SK-175/96	1.17	1.65	0.84	1.53	13.13	4.07	0.031	0.63	106	0.716333	19.9	0.512066	-11.2	78
SK-175/100	0.97	1.94	0.59	1.97	16.19	5.12	0.033	0.70	78	0.721181	22.0	0.512051	-11.5	82
SK-175/103	0.74	1.50	0.46	1.03	7.30	4.86	0.033	0.45	65	0.723240	22.5	0.511955	-13.3	73
SK-175/108	0.47	1.99	0.27	1.48	15.68	5.45	0.025	0.75	50	0.733000	23.6	0.511880	-14.8	85
SK-175/115	0.61	1.89	0.29	1.14	13.19	3.60	0.027	0.74	48	0.732160	26.8	0.511870	-15.0	83
SK-175/118	0.17	0.94	0.12	0.39	2.63	1.51	0.010	0.20	17	0.738966	6.8	0.511827	-15.8	68
SK-175/120	0.11	0.45	0.09	0.30	0.87	0.67	0.005	0.11	10	0.738400	4.3	0.511753	-17.2	57
SK-175/123	0.18	0.75	0.12	0.86	2.56	1.99	0.013	0.41	16	0.742183	16.5	0.511763	-17.1	71
SK-175/129	0.92	1.98	1.34	2.34	16.86	6.02	0.039	0.75	65	0.721891	18.7	0.511951	-13.4	80
Yangon R. SPM	0.81	1.96	0.47	2.66	22.68	8.66	0.051	1.14	70	0.716716	26.2	0.512171	-9.1	87
Salween R. BL	0.88	1.93	0.54	1.23	11.51	4.46	0.029	0.80	70	0.731794	21.3	0.511885	-14.7	77
Salween R. SPM	0.96	1.92	0.51	1.15	10.31	4.08	0.027	0.67	72	0.731435	22.9	0.511847	-15.4	75

R: River; **BL**: Bed load; **SPM**: Suspended particulate matter, $\varepsilon_{Nd}(0)$: ε_{Nd} at present time

192 | Page

The ⁸⁷Sr/⁸⁶Sr and ε_{Nd} values of shelf sediments vary from 0.712245 to 0.742183 and -6.29 to -17.25 respectively. Higher ε_{Nd} values were found for samples from the Western Myanmar coast, which usually have low ⁸⁷Sr/⁸⁶Sr. Sediments collected from Mergui shelf region have most radiogenic Sr and least radiogenic Nd, similar to those reported in the Ganga–Brahmaputra Rivers (Galy and France-Lanord, 2001). Sediments from off Salween River contain higher ⁸⁷Sr/⁸⁶Sr and lower ε_{Nd} . Sr and Nd isotope compositions of sediments collected from the Gulf of Martban are intermediate to the two extremes defined by sediments of the Arakan (Rakhine) coast and that of the Salween mouth and the Mergui shelf. The Irrawaddy and the Salween River sediments have contrasting Sr and Nd isotope composition; Irrawaddy has lesser radiogenic Sr and more radiogenic Nd when compared to that of the Salween. Sr and Nd isotope compositions of the Salween sediments are comparable to that of the lower Meghna (Combined Ganga and Brahmaputra, G–B) in Bangladesh (Galy and France-Lanord, 2001).

5.2.1 Major Element Compositions and Implications for Provenance

In this study chemical composition has been determined in the silicate fraction of the sediments. Al and Fe display large variability in these sediments. Part of these variabilities result from their source effect whereas weathering and size sorting introduce a part of it. Al in these sediments varies linearly with K, Mg, Fe, and Ti with a correlation coefficient (r for number of samples n = 46) 0.79, 0.86, 0.74, and 0.73, respectively, however, there is a very poor correlation of Al with Na (r = 0.31 for n = 46) and Ca (r = 0.01 for n = 46). These correlations could be due to the dominance of ferromagnesian silicates in the source regions followed by weathering and transport causing loss of mobile element sand size sorting. The statistically significant relationship between iron and aluminum suggests that iron oxides are not important since Fe is associated with aluminum in aluminosilicate phases (Alagarsamy et al., 2010). Lack of
correlation of Ca and Na with Al in these sediments results from preferential loss of these mobile elements with respect to Al during chemical weathering. Ti is very less abundant but shows a significant positive correlation with Al due to similar source, chemical behavior, and size sorting. K is more abundant in feldspar and illite so that the variations in the K/Al ratio may reflect the variations in feldspar and illite abundances present in the sediments due to inherent source signature or due to weathering and transport. Higher K concentration shows more feldspar and illite (Colin et al., 1999; Singh et al., 2008) in these sediments. On FM-CN-K ($Fe_2O_3 + MgO - CaO + Na_2O - K_2O$) diagram (Fig. 5.2A) a large number of samples plot toward FM apex confirming their ferromagnesian affinity which is further supported by good positive correlation (r = 0.81 for n = 46) between Fe and Mg. Mafic rocks such as basalts/ophiolites present in the drainage of the upper Irrawaddy catchment, in the central trough and in the Indo-Burman-Arakan (IBA) ranges could be an important source of sediments to the Andaman Shelf even though they occupy only small fraction of the Irrawaddy catchment. On A-CN-K ($Al_2O_3 - CaO + Na_2O - K_2O$) ternary plot (Fig. 5.2B) the majority of samples of the Andaman Shelf plot parallel to A-CN join, indicating progressive chemical weathering of the samples originating from mafic compositions. Variable chemical weathering of these sediments is also reflected by their variable Chemical Index of Alteration (CIA = $[Al_2O_3/(Na_2O + K_2O + CaO + Al_2O_3)] \times$ 100; Nesbitt and Young, 1982). CIA values of the Andaman Shelf sediments range between 53 and 88% (Table 5.1), suggesting significant variation in their chemical weathering. Few samples collected around the Mergui Shelf region contain very low concentrations of all the major elements analyzed in this study; this could be due to the fact that they are coarse-grained sands (Rodolfo, 1969) mostly dominated by quartz.



Fig. 5.2: (A) FM-CN-K and (B) A-CN-K ternary plots of Andaman Shelf sediments. Numbers within the ternary plots indicate the sample numbers. Values for the basalts, granites, Upper crust (UC), Post-Archean Australian Shale (PAAS) and North American Shale Composite (NASC) are also plotted (Taylor and McLennan, 1985). The FM-CN-K plot suggests mafic lithology as the dominant source of the majority of the sediments which have undergone through variable chemical weathering evolving toward Al_2O_3 apex (A-CN-K plot).

5.2.2 Provenance Tracing Using Sr and Nd Isotopic Systematics

Sr and Nd concentrations and their isotope compositions in the Andaman Shelf sediments were analyzed in their silicate phases. ⁸⁷Sr/⁸⁶Sr ratios in these sediments show significant variations, ranging between 0.712245 and 0.742183. Their Sr concentrations lie between 10 and 162 μ g g⁻¹. Nd concentrations and $\varepsilon_{Nd}(0)$ in these shelf sediments vary from 2.4 to 38.6 µg g⁻¹ and -6.29 to -17.25 respectively. ⁸⁷Sr/⁸⁶Sr ratios of surface-slurry and bank sediments at the mouth of the Salween River are 0.731794 and 0.731435 with Sr concentrations, 70 and 72 $\mu g g^{-1}$ and their $\varepsilon_{Nd}(0)$ are -14.69 and -15.43 with Nd concentrations, 21.3 and 22.9 μ g g⁻¹ respectively. Sediment collected at the mouth of the Yangon River, a distributary of the Irrawaddy River has 87 Sr/ 86 Sr ratios and $\epsilon_{Nd}(0)$ 0.716716 and -9.11 with their Sr and Nd concentrations 70 and 26.2 µg g⁻¹ respectively. Majority of the samples from the Andaman Shelf have ⁸⁷Sr/⁸⁶Sr ratios between 0.712245 and 0.733000 and $\varepsilon_{Nd}(0)$, -9.11 and -15.43 with Sr and Nd concentrations around 75 μ g g⁻¹ and 25 μ g g⁻¹ respectively. Few samples collected close to Arakan Coast have lower ⁸⁷Sr/⁸⁶Sr ratios, 0.716734–0.713101 and higher radiogenic Nd, $\varepsilon_{Nd}(0)$ values -6.29 to -7.21 respectively, reflecting their Indo-Burman ranges association (Licht et al., 2013). A few samples collected close to Mergui Archipelago have high radiogenic ⁸⁷Sr/⁸⁶Sr ratios, 0.738400–0.742183 and low $\varepsilon_{Nd}(0)$, -15.82 to -17.25. These radiogenic Sr and non-radiogenic Nd are similar to those reported for the sediments of delta region of the Lower Meghna (combined G–B; Galy and France-Lanord, 2001), however, it is quite unlikely to get G-B sediments at this location, this region being very far from the G-B reaches and lying away from their sediment transport pathways.

 87 Sr/ 86 Sr ratio and ϵ_{Nd} of sediments from the various river and ocean basins have been used successfully to track their sources (Goldstein and O'Nions, 1981; Bouquillon et al., 1990; France-Lanord et al., 1993; Galy et al., 1996, 2010; Winter et al., 1997; Pierson-Wickmann et al., 2001; Clift et al., 2002; Singh and 196 | P a g e France-Lanord, 2002; Banner, 2004; Ahmad et al., 2005, 2009; Colin et al., 2006; Singh et al., 2008; Viers et al., 2008; Rahaman et al., 2011; Tripathy et al., 2011; Goswami et al., 2012; Awasthi et al., 2014; Ali et al., 2015). These isotope pairs are used as reliable proxies to track the sediment sources, as there are distinct differences in their composition in the different lithologies supplying these sediments. However, successful tracking of the sediment sources using Sr-Nd isotope pair depends to a great extent on their preservation during their weathering and transport. Weathering and transport of the sediments may influence the isotope composition of Sr compared to that of Nd due to mobile nature of the former, making the Nd isotope composition more robust provenance tracer (Walter et al., 2000; Tutken et al., 2002).



Fig. 5.3: Scatter plot of ⁸⁷Sr/⁸⁶Sr and ε_{Nd} with Al₂O₃ (wt. %; A, C) and CIA (B, D) of the shelf sediments. The absence of any correlations (r = 0.04-0.5 for n = 46) among them suggests that Sr and Nd isotope compositions of these sediments are not influenced by size sorting and chemical weathering and hence can be used as good proxies to constrain their sources.

Robustness of Sr and Nd isotope compositions in tracking the sediment sources in the Andaman Shelf can be verified by observing their relation with Al and chemical index of alteration (CIA) as they get influenced by the processes of size sorting and chemical weathering respectively which might affect the isotope composition of Sr and Nd of these sediments (Singh et al., 2008). ⁸⁷Sr/⁸⁶Sr and ε_{Nd} of the sediments of Andaman Shelf have been plotted with their Al contents and CIA in Fig. 5.3A-D. These scatter plots do not show any interrelation among Sr-Nd isotope composition, Al contents and CIA of the sediments, suggesting the minimal influence of weathering and transport on these isotope compositions and hence they can be used quite reliably to track the sources of these sediments.

Fig. 5.4A and B shows the distribution patterns of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ϵ_{Nd} in the Andaman Shelf. These distribution patterns show three distinct zones with their characteristic Sr-Nd isotope signatures. The first zone, comprising the Western Myanmar Shelf region along Arakan Coast and around the mouth of the Irrawaddy River, is characterized by lower 87 Sr/ 86 Sr and higher ε_{Nd} . This zone probably gets sediments through Kaladan, Naf and other smaller rivers draining the IBA ranges having 87 Sr/ 86 Sr ratios, 0.714-0.718 and $\varepsilon_{Nd}(0)$, -7.8 to -3.9 (Licht et al., 2013) and through Irrawaddy Rivers. The second zone is the area around the mouth of the Salween River with higher 87 Sr/ 86 Sr and lower ε_{Nd} and gets sediments from the Salween River. The third zone is characterized by distinctly high $^{87}\text{Sr}/^{86}\text{Sr}$ and low ϵ_{Nd} around the Mergui Archipelago in the Southern Myanmar. The Sr-Nd isotope composition of these sediments is very similar to those of the Lower Meghna (Galy and France-Lanord, 2001). The sediments from the GBR system may come to the Andaman Shelf and to the Mergui Archipelago region through the North/South Preparis Channel. It is, however, very difficult to envisage GBR sediments reaching such far a location without impacting the sediments of shelf region around the mouth of the Irrawaddy. Eastern Andaman Shelf sediments do not show affinity with those from the Irrawaddy and the



Fig. 5.4: Distribution patterns of (A) 87 Sr/ 86 Sr and (B) ϵ_{Nd} in the Western Myanmar, Northern and Eastern Andaman Basin. Both these patterns indicate four dominant sources of sediments, (i) rivers from the Arakan Coast, (ii) The Irrawaddy River, (iii) the Salween River, and (iv) the Tanintharyi and other smaller rivers draining Southern Myanmar.

End-member	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr Mean (SD)	$\epsilon_{ m Nd}$	ε _{Nd} Mean (SD)	References
Ganga- Brahmaputra	0.7379 to 0.7530	0.7455 (0.0107)	-14.8 to -17.4	-16.1 (1.8)	Galy and France-Lanord, 2001.
Indo-Burman- Arakan	0.7050to 0.7180	0.7101 (0.0037)	0.3 to -8.0	-5.2 (2.7)	Colin et al., 1999; Allen et al., 2008; Najman et al., 2008; Licht et al., 2013.
Irrawaddy River	0.7080 to 0.7135	0.7129 (0.0031)	-8.3 to -12.2	-10.3 (1.6)	Colin et al., 1999; Allen et al., 2008; Present Study.
Salween River	0.7314 to 0.7318	0.7316 (0.0003)	-14.7 to -15.4	-15.1 (0.5)	Present Study.
Southern Myanmar / Western Thailand	0.7256 to 0.8272	0.7685 (0.0264)	-23.0 to -27.3	-25.4 (1.5)	Nakapadungrat et al., 1984; Liew and McCulloch, 1985.

Table 5.2: The end-members of Northern Andaman Shelf sediments, with their isotopic properties

Salween Rivers either. These sediments, therefore, require another source. Close inspection of lithologies around the Mergui Archipelago and very few available isotope data for them suggest that the granites from the Central and Western belts with higher ⁸⁷Sr/⁸⁶Sr and lower ε_{Nd} (Nakapadungrat et al., 1984; Liew and McCulloch, 1985) present in the Southern Myanmar and Western Thailand could be the possible source of these sediments. The Tanintharyi, Tavoy and other smaller rivers flowing these granitic belts could possibly be bringing sediments around the Mergui Archipelago. Part of sediments in this region might originate from the

erosion of several small islands of the Mergui Archipelago itself. Granites of the Southern Myanmar and Western Thailand were not known to be a major source of sediments to the Andaman Shelf earlier. This study however, identifies these granitic belts as an important source of sediments to the Eastern Andaman Shelf in Southern Myanmar.

To further identify the sources of sediments of the Andaman Shelf, their Sr and Nd isotope compositions have been plotted on two isotopes mixing diagram (Fig. 5.5). There could be five potential sources of sediments of the Andaman Shelf: (i) Rivers draining the IBA Ranges with low ⁸⁷Sr/⁸⁶Sr and high $\varepsilon_{\rm Nd}$, (ii) Irrawaddy River with low ${}^{87}{\rm Sr}/{}^{86}{\rm Sr}$ and high $\varepsilon_{\rm Nd}$, (iii) Salween River with higher 87 Sr/ 86 Sr and low ε_{Nd} , (iv) G–B river system with high 87 Sr/ 86 Sr and low ϵ_{Nd} and (v) Rivers draining the Southern Myanmar and Western Thailand with high 87 Sr/ 86 Sr and low ε_{Nd} . The Sr and Nd isotope compositions of the possible dominant end-members (Table 5.2) are also plotted. The isotope compositions of these end-members (Table 5.2) are assigned based on those available in the literatures and based on few samples of the Irrawaddy and the Salween Rivers analyzed this study. Due to lack of study in Myanmar and adjoining areas, isotope values of some of the end-members need to be fixed either using the few available data or indirectly. There is no data available on the smaller rivers flowing through the western slopes of the IBA ranges along the Arakan Coast. Sr-Nd isotope compositions for the lithologies present in Indo-Burman ranges (Licht et al., 2013) have been considered for these rivers (Colin et al., 1999). Sr, Nd isotope compositions of two sediment samples of unknown locations of the Irrawaddy River is available in the literature (Colin et al., 1999; Allen et al., 2008). In this study, one sediment sample from the mouth of the Yangon, one of the distributaries of the Irrawaddy River, was analyzed for its Sr and Nd isotope compositions which are consistent with the earlier reported values. Irrawaddy end-member is based on these three data (Table 5.2). The Salween end-member is characterized by Sr and Nd isotope composition of two sediment samples 201 | Page

collected from its mouth and analyzed in this study (Table 5.2). The Sr isotope value of this end-member is supported by high ⁸⁷Sr/⁸⁶Sr observed in granites present in its catchment (Nakapadungrat et al., 1984).



Fig. 5.5: Binary mixing plot of Sr and Nd isotope composition of the sediments of the Andaman Shelf. Sr and Nd isotope compositions of the potential end-members are also shown. For details about these end-members please see the text. This plot suggests that majority of the sediments to the Andaman Shelf are derived from the Irrawaddy River along with the Salween and rivers flowing through the western slopes of the Indo–Burman–Arakan and Western/Central granitic ranges. Blue curve represents the hyperbolic two end member mixing curve where as ticks on them indicate the fractions of the end members.

Fixing the end-member values for sediments brought by the Tanintharyi, the Tavoy and other smaller rivers in Southern Myanmar was difficult as these rivers have never been analyzed and data are not available. As these rivers mostly flow through the Western/Central granitic belts (Fig. 5.6), the few data available on these granites on Sr and Nd isotopes from the Southern Myanmar and Western Thailand (Nakapadungrat et al., 1984; Liew and McCulloch, 1985) have been used to constrain this end-member (Table 5.2). The end-member values of the Ganga–Brahmaputra River are based on the data of the Lower Meghna (Galy and France-Lanord, 2001). On the Sr-Nd isotope mixing diagram (Fig. 5.5), samples collected from the shelf area along Arakan Coast show an affinity toward IBA end-member suggesting that the rivers such as the Kaladan, Naf and other small rivers flowing through the Arakan Coast deliver sediment to the nearby shelf. Impact of the G–B river system on the Western Myanmar Shelf sediments seems to be quite minimal, if any, despite their proximity with the G–B delta. The eastward surface current flowing from the G–B delta toward this shelf is unable to bring an appreciable amount of sediments from the G-B delta to the Western Myanmar Shelf. Sr and Nd isotope composition of several samples plot near the Irrawaddy end-member suggest that this river is the major source of sediments to the Andaman Shelf. Sediments from the Gulf of Martban are a mixture of sediments derived from the Irrawaddy and the Salween Rivers in more or less an equal proportion. Further south-east, near the mouth of the Tavoy River, sediments of the Irrawaddy origin are still present, though in lesser fraction compared to the Gulf of Martban. Sediments from the shelf around the South Myanmar are quite unique. They have high 87 Sr/ 86 Sr and low ε_{Nd} , similar to those from the G-B river system in the Bangladesh. As discussed above, G-B sediments cannot reach near the Mergui Archipelago and majority of these sediments are derived from the erosion of the granitic belts from the Southern Myanmar and Western Thailand. These are a mixture of sediments derived from the Tanintharyi, the Irrawaddy, and the Salween Rivers. It is almost clear from Fig. 5.4 and 5.5 that G–B river system contributes very little sediments to the Andaman Shelf. It is unlikely that Bengal shelf sediments are reaching the Andaman Shelf in recent times.



Fig. 5.6: The average rainfall (cm y⁻¹) pattern for the 5 years (January 1998 to December 2002) over the present study area. Please note the intensely focused precipitation (~5 m y⁻¹) over the western slopes of the Indo–Burman–Arakan ranges along the Rakhine coast and over the western slope of Western/Central granitic ranges in Southern Myanmar (Source: <u>http://trmm.gsfc.nasa.gov/</u>).

5.2.3 Control on Erosion Determining the Sediment Sources

It is borne out from the above discussion that majority of the sediments in the Andaman Shelf are derived from (i) the Irrawaddy River, (ii) the Salween River, (iii) IBA ranges through the rivers of the Arakan Coast and (iv) Central and Western granite belts in the Southern Myanmar and Western Thailand through the Tavoy, the Tanintharyi and other smaller rivers (Fig. 5.1). Large sediment supply from the IBA ranges through smaller rivers of western slopes of the IBA and through the Irrawaddy and Southern/Western granitic belts suggest significantly higher erosion rates over them. Observation of high erosion over the IBA ranges was suggested earlier by Colin et al. (1999). However, high erosion over the Western/Central granitic belt is reported for the first time in this study. Higher erosion over these two ranges seems to be controlled by the intense and focussed precipitation and topography (relief). Annual rainfall over the IBA and Western/Central granite ranges is as high as 5 m (Fig. 5.6), much higher compared to other regions providing sediments to the Andaman Shelf. Most of this rainfall occurs during the south-west monsoon. Further, the high and focussed precipitation coincides with higher relief on western slopes (Fig. 5.7) of these ranges. Rainfall and elevation along the transects following the SW monsoon tracks, two over the IBA and one over the Southern/Western granite ranges are plotted in the Fig. 5.7. Along all these sections, high and focussed precipitation coincides with higher relief along the western slopes of these ranges causing higher stream power leading to higher erosion. Such higher erosion due to focussed precipitation on higher relief on the southern slopes of the Higher Himalaya has been reported earlier too (Singh and France-Lanord, 2002; Hodges et al., 2004; Thiede et al., 2004; Wobus et al., 2005; Singh, 2006; Singh et al., 2008). Thus, the sediment budget of the Andaman Shelf, in addition to the Himalayan-Tibetan ranges, is controlled by erosion over the Indo-Burman-Arakan and Western/Central granitic ranges due to intense and focussed precipitation over the higher relief of their western slopes.



Fig. 5.7: Precipitation and elevation plotted along the three transects shown on DEM map following the SW monsoon track. Intense and focused precipitations over the higher relief of the western slopes of the IBA (Transects AA', BB') and Western/Central granitic ranges (Transect CC') cause higher erosion in these catchment (Source: http://dwtkns.com/srtm/ and <u>http://trmm.gsfc.nasa.gov/</u>).

5.2.4 Role of Sea-Surface Current in Controlling the Sediment Dispersion

The sea-surface current of the Andaman Sea observes two reversals. It flows eastward during SW monsoon and westward during NE monsoon (Fig. 5.1). As most of the precipitation occur during the south–west monsoon causing higher erosion leading to ~90% of annual sediment discharge, therefore eastward current from the BoB and from the shelf along the Arakan Coast brings sediments to the Northern Andaman Shelf which mix with sediment brought by the Irrawaddy River and get deposited on the shelf. These sediments get transported further eastward and mix with sediments from the Salween and get deposited in Gulf of Martban and on the eastern shelf (Fig. 5.1). These currents bring sediments from the Irrawaddy and the Salween Rivers further to the south which get deposited after mixing with sediments brought by the Tavoy and the Tanintharyi Rivers. During the north–east monsoon the sea-surface current in the Andaman Sea reverses and flows westward (Fig. 5.1). However, low precipitations during NE monsoon leads to less erosion in the catchment and hence lower sediment delivery to the shelf. Part of the sediments deposited on this shelf during SW monsoon gets transported westward to the Eastern BoB during NE monsoon (Colin et al., 1999; Ramaswamy et al., 2004).

5.3 Conclusion

Major element and Sr and Nd concentrations and their isotope compositions have been determined in the silicate fraction of the sediments deposited on the Northern and Eastern Andaman Shelf to constrain their sources and factors influencing their erosion, dispersal, and deposition. Major element compositions of the majority of these sediments indicate their ferromagnesian nature which is sourced from mafic lithologies present in the drainage of the Irrawaddy River and over the IBA. Sr and Nd isotope compositions of Andaman Shelf sediments suggest that these sediments are mostly derived from (i) the Irrawaddy River, (ii) the Salween River, (iii) the IBA ranges either through the smaller rivers flowing through the Arakan coast or through the Irrawaddy River whose western tributaries such as the Chindwin etc. draining these ranges and (iv) the Western/Central granitic belts of the Myanmar and Thailand through the Tavoy, the Tanintharyi and other smaller rivers. The erosion and sediment delivery from these sources are controlled by the intense and focussed precipitation over the high relief on the western slopes of these ranges and further dispersed by the eastward sea-surface current controlled by SW monsoon on the Northern and Eastern Andaman Shelf. This study for the first time recognizes the higher erosion on the western slopes of the granitic ranges of the Southern Myanmar, supplying a significant amount of sediment to the Eastern Andaman Shelf around the Mergui Archipelago.

Chapter 6

Dissolved Hf and Nd concentration and their isotopic compositions in the Indian Ocean: Implications to waterparticles interaction, upwelling, water mass mixing and their sources

6.1 Introduction

Global ocean circulation plays a key role in controlling and regulating the Earth's heat, carbon and oceanic nutrient budgets. Furthermore, ocean circulation helps in regulating various other properties of seawater such as concentrations of the dissolved oxygen (DO), trace elements and isotopes (TEIs) by transporting them from one ocean basin to another. As a consequence, by studying the water masses in the ocean, the rate and transport properties within the ocean can be understood. The conventional temperature-salinity (T-S) diagrams, nutrients and the geochemical trace elements (Fe, Mn, Cd, Ba, Zn), stable isotopes (δ^{13} C) and radiogenic isotopes of Hafnium (Hf) and Neodymium (Nd) provide good proxies to study ocean circulation as their distributions are governed by mixing processes in the ocean. Unlike T-S, Nutrients, δ^{13} C, and some the trace metals; isotopic compositions of Hf and Nd cannot be modified by evaporation, precipitation, chemical and biological processes (Piepgras et al., 1979; Frank et al., 2002; Goldstein and Hemming, 2003; Godfrey et al., 2009; Rickli et al., 2009, 2010, 2014; Zimmermann et al., 2009a, b; Stichel et al., 2012). Thus, these isotopic compositions are conservative in the water column. Therefore, concentration of dissolved rare earth elements (REEs), radiogenic Hf and Nd isotopes are extensively used as water-mass proxies to examine their sources and to study paleo and modern ocean circulations. Moreover, the residence time of Hf and Nd in the ocean is of the order of or less than ocean mixing time (~500-1500 years) making them suitable proxies of ocean water circulation. The residence time of Hafnium in seawater is marginally higher (1000-1500 years) than that of Neodymium (500-1000 years; Jeandel, 1993; Jeandel et al., 1995; Godfrey et al., 1997; Lee et al., 1999; Tachikawa et al., 1999; David et al., 2001; Frank, 2002). The distribution of Hf and Nd isotopes in the oceans can be used to reconstruct the ocean circulation as the pattern and rate of ocean circulation generates spatial variation in these isotopes. Therefore, the Hf and Nd isotopic composition of water masses are one of the best proxies to study the ocean circulation due to their

suitable residence time and nature to acquire and preserve the source signature. There have been a few studies on the concentration of REEs, Nd isotopic composition of seawater, primarily focused in the Arctic, Atlantic, and the Pacific Oceans (Piepgras et al., 1979; Jacobsen and Wasserburg, 1980; German and Elderfield, 1990; Bertram and Elderfield, 1993; Jeandel, 1993; Jeandel et al., 1998; Amakawa et al., 2000, 2004; Goldstein and Hemming, 2003; Nozaki and Alibo, 2003; Godfrey et al., 2009; Rickli et al., 2009, 2010, 2014; Zimmermann et al., 2009a, b; Stichel et al., 2012; Haley et al., 2014; Hathorne et al., 2015). Very little is known about the water mass structure and various water masses present in the Indian Ocean, particularly that of deep waters in the northern Indian Ocean (Amakawa et al., 2000; Nozaki and Alibo, 2003; Singh et al., 2012; Goswami et al., 2014). The limited studies on Nd isotopic composition of seawater from the Indian Ocean suggest that it is intermediate to that of the Atlantic and the Pacific Oceans. The Hf isotopic study is far more limited than the study of Nd isotopes in the ocean, mainly due to difficulties in its measurement (Godfrey et al., 2009; Rickli et al., 2009, 2010, 2014; Zimmermann et al., 2009a, b; Stichel et al., 2012).

Hf isotopic composition exhibits large variability in the erosion products during continental weathering as the resistant mineral like zircon (with low Lu/Hf) selectively retains unradiogenic Hf (Lee et al., 1999; Frank, 2002; Goldstein and Hemming, 2003). The Hf in zircons of the sand fraction is almost unavailable to weathering and erosion and is not introduced into seawater. Therefore, the seawater data, either measured directly or inferred from ferromanganese crust has higher ε_{Hf} for a given ε_{Nd} (Godfrey et al., 1997; Albare`de et al., 1998; Lee et al., 1999; Piotrowski et al., 2000; David et al., 2001; Van de Flierdt et al., 2002, 2004a, b, 2007, 2016, Rickli et al., 2009, 2014). In this study, concentration of Nd, Hf and their isotope compositions are being used to study the ocean circulation, to identify the water masses present in the Arabian Sea and the North-eastern Indian Ocean and to quantify the additional sources of Nd in the Arabian Sea using inverse modeling.

6.1.1 Evolution of Hafnium and neodymium isotopes

The radiogenic isotope compositions of Hf and Nd in ocean waters exhibit large variations due to their various input sources. These isotope compositions serve as tracers of past and modern oceanographic circulation patterns and the provenance of rocks and their weathering inputs resulting from tectonic and climatic factors (Frank, 2002; Goldstein and Hemming, 2003). The radiogenic Hf and Nd isotope compositions in a geological sample are regulated by the decay of their associated parent isotopes. The radiogenic ¹⁷⁶Hf isotope results from the beta (B) decay of 176 Lu (Lutetium) with a half-life (t_{1/2}) of 37.1 billion years, and is described as a ratio to stable isotope ¹⁷⁷Hf. Similarly, ¹⁴³Nd isotope outcome of ¹⁴⁷Sm (Samarium) from the alpha (α) decay with a half-life (t_{1/2}) of 106 billion years, is narrated as a ratio to stable isotope ¹⁴⁴Nd (Faure, 1977; Frank, 2002; Goldstein and Hemming, 2003; Rickli et al., 2009). The mineralogical process and the age of the sample since crystallization, regulate the parent/daughter abundances ratios and hence the radiogenic isotopic composition of the sample. Therefore, the radiogenic isotope composition of any geological/environmental sample is governed by the parent/daughter abundances ratio, a function of mineralogical processes, and the age of the sample since crystallization (Faure, 1977). Owing to their similar geochemical nature, in general fractionations of Lu/Hf and Sm/Nd ratios are well-correlated in geological processes. Hence, ¹⁷⁶Hf/¹⁷⁷Hf and ¹⁴³Nd/¹⁴⁴Nd ratios of given geological samples show a strong positive correlation (Faure, 1977; Frank, 2002; Goldstein and Hemming, 2003; Rickli et al., 2009).

The Hf and Nd isotope evolution over geological time scale has been shown in Fig. 6.1. The elemental fractionation of Lu/Hf and Sm/Nd causes isotopic evolution of the depleted magma source and the continental crust differently during igneous processes. For example, Nd and Hf are slightly less compatible than Sm and Lu, resulting in a relative enrichment of Nd and Hf in

crustal melts. The continental crust, therefore, has low $^{143}Nd/^{144}Nd$ (ϵ_{Nd}) and $^{176}Hf/^{177}Hf$ (ϵ_{Hf}) ratios compared to mantle (Fig. 6.1).



Fig. 6.1: The Hf and Nd isotope evolution over geological time scale. During igneous processes the elemental fractionation of Lu/Hf and Sm/Nd forms various isotopic compositions from the depleted magma source and the continental crust, modified after, Faure, (1977).

6.1.2 Hydrology of the Indian Ocean

The Indian Ocean is surrounded by the Asian, Australian, Antarctic and the African continents and also placed in between the Atlantic, Antarctic and the Pacific Oceans (Fig. 6.2). The Indian Ocean can be considered as two parts, divided by the equator viz. Northern and Southern Indian Ocean. The Arabian Sea, Bay of Bengal (BoB) and the Andaman Sea constitute the Northern Indian Ocean and receive huge dissolved and particulate fluxes from the Himalayan and other fluvial river systems such as the Indus, Ganga-Brahmaputra (G-B), Irrawaddy, Salween, Godavari, Mahanadi and the Narmada (Fig. 6.2). Aeolian dust from the nearby landmasses also contributes significant TEIs fluxes (Fig. 6.2). There are no such major riverine sources available to the Southern Indian Ocean; however, it receives dominant dissolved and particulate flux from the Australian and African continents. The Indian Ocean also contains various water masses received from different ocean basins such as low salinity BoB surface waters, Pacific Ocean waters through Indonesian Through Flow (ITF), NADW and AABW. The detailed water masses existing in the Indian Ocean are described below.

6.1.3 North-eastern and Southern Indian Ocean water masses

The BoB and the Andaman Basin lie within the Northern Indian Ocean and are alienated by Andaman-Nicobar Ridge. In general, the surface waters of the BoB have low salinity due to the dilution by monsoonal precipitation and the high fresh water discharge from the G-B, Godavari, Mahanadi, Krishna, Kaveri and other Indian Rivers. In addition to these fresh waters, the less saline Indonesian Through flow (ITF) waters enter into the southern BoB through an eastward Equatorial Jet (EJ) during the inter-monsoon (Shenoi et al., 1999). This leads to the depletion of salinity in the southern BoB surface waters. In the BoB, the high precipitation over evaporation leads to the minimum biological productivity and week oxygen minimum zone as compared to the Arabian Sea. The surface waters in the BoB also receive a considerable amount of aeolian dust particles from the nearby landmasses. Both of North-East (NE) and South-West (SW) monsoons are active in the BoB.



Fig. 6.2: The cruise tracks and sampling locations in the Indian Ocean. The numbers shown in the figure represent the sampling locations in the Arabian Sea (SS 300 during April-May, 2012; continuous blue line) and Indian Ocean (SK 304 during March-May, 2013; dashed red line) for trace elements and isotope (TEI) study to establish the existing water masses and their sources.

The average depth of the Andaman basin has been reported to be about 2000 m (Rodolfo, 1969; Ramaswamy et al., 2004; Rao et al., 2005). The Andaman basin receives the dissolved and particulate fluxes primarily from the Himalayan Rivers such as the Irrawaddy and the Salween (Robinson et al., 2007; Chapman et al., 2015). The higher erosion also provides the dissolved and

particulate matters through the rivers draining the western slope of the Southern Myanmar and Western Thailand such as the Fly, Tanintharyi and the Tavoy Rivers to the Andaman basin (Damodararao et al., 2016). The Andaman Sea also receives the low salinity surface waters from the BoB through NE and SW monsoons (Fig 6.2; Rodolfo, 1969; Rao et al., 2005).



Fig. 6.3: The measured potential temperature vs. salinity (θ -S) plots for the waters sampled in the Indian Ocean onboard ORV SK-304. The dashed lines show the potential density (σ_{θ}) contours for the various water masses existing in the Indian Ocean. The significant presence of BoBs, IW, ASHSW, NIIW and IIW water masses in the profiles sampled are seen. The deep and bottom water masses are composed with MNADW and AABW.

The surface waters of the BoB and the Andaman basin are lower in salinity and higher in temperature. The potential temperature and salinity of the deep waters in both the BoB and the Andaman Basin relate with that of the Equatorial Indian Ocean waters (Fig. 6.3). The several water masses have been distinguished in the BoB and the Andaman Basin water column (Singh et al., 2012). The existing major water masses in the Indian Ocean have been distinguished using the conventional potential temperature-salinity (θ -S) diagrams, shown in Fig. 6.3. The temperature and salinity of waters near the equator in the Indian Ocean are similar to those in the Pacific and Atlantic Oceans (Rodolfo, 1969).

6.1.4 The Arabian Sea water masses

The Arabian Sea, limited in the northern Indian Ocean, experiences the seasonally reversing monsoonal winds. The Arabian Sea is also characterized by the presence of oxygen minimum zone (OMZ) in its intermediate waters resulting from the high productivity in the region sustained by upwelling during monsoon. It receives a significant amount of dissolved and particulates from the rivers such as the Indus, Narmada, Tapi and other west flowing rivers along with atmospheric dust from bordering arid landmasses (Fig. 6.2). In last two decades, several studies on the Arabian Sea conclude that several water masses exist in it (Wyrtki, 1973; Shenoi et al., 1993; Dileep Kumar and Li, 1996; You, 2000; Schott and McCreary, 2001; Goswami et al., 2014). The surface waters in the Arabian Sea are composed of two water masses, the Arabian Sea High Salinity waters (ASHSW) and the Bay of Bengal surface waters (BoBSW) in the northern and the southern Arabian Sea, respectively. Excess evaporation over precipitation in the Northern Arabian Sea leads to formation of ASHSW and circulates towards the southern Arabian Sea. On an average, the core of the ASHSW is observed between 50 and 100 m depth (Shenoi et al., 1993). The salinity of this water mass varies from 35.0-36.5, whereas their potential temperature is in the range of 27 \pm

2 °C (present study). Additionally, low salinity surface waters from the BoB enter into the Eastern Arabian Sea near the southern tip of India through the East India Coastal Current (EICC) and distributes over its surface; the extent of this spread dependent on monsoon intensity, particularly the NE monsoon and the discharge of a variety of rivers into the BoB. The subsurface waters up to ~100 m depth in the Arabian Sea originate from the Persian Gulf waters (PGW) with high salinity (~36.8) and low potential temperature (~12 °C) and Red Sea waters (RSW) with high salinity (~36) and very low potential temperature (~10 °C; Shenoi et al., 1993). The PGW and RSW exist in the Arabian Sea at a depth of 200 to 600 m and 200 to 1000 m, respectively. The deep and bottom waters are regulated by the North Atlantic Deep waters (NADW) and the Antarctic Bottom waters (AABW) with low salinity (\sim 34.8), low potential temperature (\sim 1.8 °C) and high potential density (Wyrtki, 1973; Mantyla and Reid, 1995; Dileep Kumar and Li, 1996; Goswami et al., 2014). Using measured potential temperature, salinity and potential density (σ_{θ}) present in the Arabian Sea water column, (θ -S- σ_{θ}) diagram is plotted to illustrate its water masses (Fig. 6.4). The existing water masses in the Arabian Sea water column have been shown in Fig. 6.4.

6.2 **Results and discussions**

Water samples have been collected from several vertical profiles of the Arabian Sea and the Indian Ocean during summer of 2012 and 2013, respectively, to construct their water masses and to understand biogeochemical processes by the analysis of their TEIs. Fig. 6.2 shows the sampling locations along with the cruise transects in the Arabian Sea and the Indian Ocean. The sampling details and methodology of the Hf and Nd concentrations and their isotopic compositions have been described in Chapter 2. The dissolved Hf and Nd concentrations were determined using isotope dilution (ID) method (Rickli et al., 2009; Zimmermann et al., 2009a, b; Stichel et al., 2012) and their isotopic compositions have been analyzed on Neptune Thermo Scientific MC-IC-PMS in Physical Research

Laboratory, India. The analyzed concentration of Hf and Nd and their isotopic compositions from several vertical profiles of the Arabian Sea and the Indian Ocean waters have been listed in Table 6.1 and 6.2. The present chapter leads the discussion on the distribution patterns and sources of dissolved Hf and Nd concentrations and ε_{Hf} - ε_{Nd} in the Arabian Sea and the Indian Ocean, finally quantifying the various water masses present in these basins.



Fig. 6.4: Potential temperature and potential density plotted over salinity $(\theta-S-\sigma_{\theta})$ in the Arabian Sea. The dashed lines show the potential density (σ_{θ}) contours for the various water masses. The South-Eastern section shows lower salinity in the surface due to incursion of lower salinity waters from the BoB. There is also a significant presence of ASHSW, RSW and PGW water masses in the sampled profiles. The deep and bottom water masses composed of MNADW and AABW are clubbed together due to the closeness of θ and S values.

Depth (m)	Salinity	θ (°C)	Nd, Pmol kg ⁻¹	٤ _{Nd}	±	
SS 300/01 (9.43 °N; 75.15 °E)						
5	34.51	29.9	19.6	-12.0	0.3	
170	35.14	15.08	15.0	-9.4	0.1	
250	35.17	12.86	12.5	-9.9	0.4	
440	35.18	10.81	13.7	-6.0	0.9	
510	35.18	10.38	-	-11.7	0.2	
600	35.19	9.83	-	-7.7	0.3	
700	35.16	9.20	16.2	-7.0	0.3	
800	35.10	8.40	-	-8.5	0.2	
900	35.06	7.68	16.7	-9.7	0.2	
1000	35.04	7.17	18.5	-8.7	0.3	
1400	34.91	5.08	19.9	-9.0	0.7	
1600	34.86	4.08	22.1	-10.0	0.4	
1800	34.83	3.32	22.9	-10.0	0.2	
2000	34.80	2.70	26.7	-8.7	0.2	
2200	34.77	2.25	-	-9.6	0.2	
2430	34.75	1.96	27.6	-10.1	0.1	
<u>SS 300/02</u>	(4.473 °N; 6	9.45 °E)				
5	34.75	29.67	13.8	-11.2	0.2	
68	35.32	25.63	-	-9.8	0.5	
75	35.29	25.08	9.1	-9.8	0.5	
150	35.28	17.59	9.9	-6.7	0.4	
250	35.15	12.76	10.1	-7.3	0.3	
340	35.12	11.59	10.7	-7.3	0.5	
470	35.12	10.45	11.2	-8.4	0.2	
560	35.15	10.10	12.5	-8.6	0.5	
670	35.16	9.60	14.2	-7.5	0.5	
780	35.17	9.12	14.3	-8.6	0.4	
900	35.10	7.87	14.4	-9.5	0.3	
1000	35.05	7.14	15.5	-8.4	0.2	
1500	34.92	4.80	-	-8.6	0.2	
2000	34.80	2.78	18.3	-8.8	0.2	
2500	34.76	1.96	20.0	-10.2	0.2	
3000	34.74	1.55	-	-8.2	0.2	

Table 6.1: Salinity, potential temperature (θ) , concentration of Nd and their isotope compositions in vertical profiles the Arabian Sea

3500	34.74	1.43	23.3	-8.6	0.2		
4350	34.74	1.39	25.2	-8.0	0.2		
<u>SS 300/03 (3.00 °N; 68.10 °E)</u>							
5	34.95	29.66	13.6	-11.3	0.4		
50	35.46	27.75	9.8	-	-		
100	35.37	21.02	7.8	-	-		
150	35.25	17.16	9.9	-	-		
200	35.34	19.81	10.2	-8.9	0.4		
300	35.11	11.79	10.6	-8.5	0.3		
390	35.07	10.25	-	-7.7	0.8		
550	35.09	9.79	11.1	-9.3	1.3		
650	35.15	9.23	11.3	-	-		
750	35.12	8.71	13.2	-5.3	1		
900	35.05	7.86	13.7	-9.0	0.4		
1000	35.04	7.14	15.2	-	-		
1300	34.91	5.40	-	-	-		
1600	34.87	4.27	15.2	-8.6	0.5		
1900	34.81	3.04	16.6	-	-		
2200	34.78	2.32	19.8	-	-		
2500	34.76	1.99	21.4	-7.5	0.5		
2800	34.75	1.71	21.3	-	-		
3100	34.74	1.55	24.3	-	-		
3470	34.74	1.41	21.5	-7.9	0.3		
<u>SS 300/04 (6.98 °N; 70.98 °E)</u>							
5	34.53	29.87	17.6	-	-		
85	36.04	27.52	7.9	-	-		
90	36.11	26.28	10.2	-	-		
100	35.92	25.03	7.7	-6.5	0.6		
150	35.04	16.15	12.9	-	-		
250	35.18	12.84	13.6	-	-		
300	35.18	12.03	10.0	-7.3	0.5		
350	35.18	11.77	-	-	-		
420	35.18	10.98	9.6	-	-		
500	35.21	10.54	11.5	-	-		
650	35.21	9.77	11.2	-7.6	0.3		
750	35.13	8.76	13.2	-	-		
900	35.08	7.78	15.8	-8.9	0.6		
1000	35.07	7.32	16.1	-	-		
1300	34.97	5.65	19.0	-	-		

1600	34.90	4.32	-	-8.0	0.8
2000	34.81	2.90	19.8	-8.6	0.7
2500	34.77	2.02	22.0	-	-
3000	34.75	1.57	23.6	-7.1	0.9
<u>SS 300/05 (</u>	11.00 °N; 6	<u>8.00 °E)</u>			
5	34.97	29.8	16.7	-8.1	0.7
100	36.28	26.13	8.8	-9.7	0.8
140	35.25	19.0	13.2	-9.4	0.4
250	35.32	16.37	-	-8.2	0.9
320	35.25	13.16	11.9	-9.0	0.4
350	35.23	11.83	-	-7.8	0.5
500	35.37	11.47	10.3	-8.4	0.8
620	35.41	10.95	11.4	-9.3	0.8
750	35.35	9.86	14.0	-8.9	0.8
900	35.26	8.74	13.4	-8.5	0.4
1000	35.20	7.99	-	-7.8	0.5
1200	35.09	6.62	16.1	-	-
1600	34.93	4.45	17.9	-9.8	0.9
2100	34.81	2.62	16.4	-8.2	0.5
2600	34.77	1.89	19.6	-8.6	2.2
3200	34.74	1.49	23.5	-8.6	0.5
3800	34.74	1.39	23.6	-	-
4020	34.74	1.34	-	-8.3	0.4
<u>SS 300/06 (</u>	12.98 °N; 6	7.98 °E)			
5	35.85	29.45	13.9	-	-
80	36.30	26.32	11.6	-7.7	0.3
160	35.43	18.40	11.0	-8.3	0.2
210	35.39	15.85	11.1	-	-
300	35.36	13.31	11.0	-	-
450	35.41	12.01	11.3	-	-
600	35.46	11.15	11.7	-	-
750	35.43	10.25	11.6	-8.0	0.2
850	35.35	9.29	12.7	-	-
1000	35.26	8.16	13.2	-	-
1200	35.13	6.79	-	-	-
1400	35.05	5.63	14.9	-8.9	0.2
1800	34.88	3.51	16.2	-	-
2200	34.80	2.44	16.8	-8.7	0.2
2700	34.76	1.79	18.8	-	-

3200	34.75	1.51	21.3	-10	0.3		
3700	34.74	1.41	23.0	-	-		
4125	34.74	1.37	25.0	-8.6	0.2		
<u>SS 300/07 (14.98 °N; 67.98 °E)</u>							
5	36.12	29.29	16.8	-8.6	0.2		
60	36.29	26.57	9.4	-7.7	0.3		
290	35.82	15.17	10.4	-7.3	0.3		
600	35.58	11.54	10.9	-8.4	0.5		
900	35.40	9.21	15.5	-8.4	0.3		
1200	35.18	6.96	15.2	-9.5	0.3		
1400	35.09	5.80	16.8	-8.9	0.2		
1800	34.89	3.61	20.1	-8.9	0.2		
2500	34.77	1.95	24.9	-8.8	0.3		
3000	34.75	1.59	20.9	-9.6	0.3		
3500	34.74	1.44	21.3	-9.5	0.3		
3880	34.74	1.40	21.8	-9.3	0.2		
4000	34.74	1.40	-	-8.9	0.5		
<u>SS 300/08 (</u>	(16.98 °N; 6	7.98 °E)					
5	36.49	29.03	12.0	-9.2	0.1		
50	36.36	27.01	9.9	-8.4	0.2		
240	35.72	16.45	10.6	-7.0	0.3		
410	35.75	13.60	10.3	-7.0	0.3		
700	35.61	11.34	10.3	-8.3	0.3		
1600	34.99	4.70	13.9	-8.4	0.4		
3000	34.75	1.58	17.7	-7.8	0.2		
<u>SS 300/09 (19.00 °N; 67.98 °E)</u>							
5	36.53	28.87	13.7	-10.2	0.3		
100	36.36	23.52	12.1	-10.7	0.4		
200	35.81	17.11	12.2	-11.3	0.1		
290	35.87	14.60	10.1	-9.1	0.3		
500	35.76	12.55	9.7	-9.6	0.3		
600	35.67	11.69	10.5	-8.5	0.3		
1000	35.38	8.48	13.4	-8.7	0.2		
1500	35.04	5.14	15.8	-8.8	0.3		
2200	34.81	2.48	16.0	-9.7	0.5		
2625	34.77	1.87	16.8	-10.0	0.3		
3200	34.75	1.52	19.7	-8.8	0.2		
<u>SS 300/10 (</u>	21.00 °N; 6	7.98 °E)					
300	35.87	15.16	10.4	-11.3	0.2		

600	35.61	11.26	9.5	-14.4	0.3		
1000	35.37	8.59	-	-12.2	0.3		
1800	34.92	3.77	15.2	-13.3	0.3		
<u>SS 300/11 (19.98 °N; 69.48 °E)</u>							
10	36.33	28.99	14.6	-13.2	0.5		
<u>SS 300/14 (19.98 °N; 71.00 °E)</u>							
10	35.87	28.64	33.9	-8.7	0.2		

-: Not Analyzed

6.2.1 Dissolved Nd concentrations in the Arabian Sea: Their sources and input mechanism

The analyzed dissolved Nd concentrations in the Arabian Sea vertical profiles vary from 7.8 to 48.6 pmol kg⁻¹ (Table 6.1). The lowest Nd concentrations are observed in the subsurface of the Southern Arabian Sea, whereas, the highest Nd concentrations are found in the surface waters of the Northern Arabian Sea near the shelf (Table 6.1). The Nd concentrations in the Arabian Sea waters along with the salinity, potential temperature and dissolved oxygen over the depth profiles have been plotted in Fig. 6.5.

The higher values of concentration of Nd in the surface waters of the Arabian Sea could be due to the interaction of water with particles coming from the Aeolian dust, shelf and fluvial sediments originating from the nearby land-masses. Subsurface waters of the Arabian Sea are characterized by lower Nd contents resulting from their removal from water column by adsorption and/or absorption on to sinking lithogenic/biological particles. The concentration of Nd in the intermediate and deep waters of the Arabian Sea increases with depth due to the re-mineralization of the scavenged particles. The concentrations of Nd in the Arabian Sea profiles are similar to those observed for the nutrients except in the surface waters (Fig. 6.5).

The seawaters near shore in the Northern Arabian Sea exhibit very high Nd concentrations, possibly on an account of dissolution of particles supplied by the Indus River. In the open ocean, towards the Eastern Arabian Sea, Nd concentrations are higher compared to the other Arabian Sea waters (Fig. 6.8a). The supply of BoB waters through East Indian Coastal Currents (EICC) in the Eastern Arabian Sea might be the reason for high concentrations of the Nd.





Fig. 6.5: The vertical profiles of salinity, potential temperature, dissolved oxygen (DO) and Nd concentrations in the Arabian Sea water column.

The dissolved Nd and Si concentrations in the Arabian Sea have been plotted with depth in Fig. 6.6. Dissolved Nd and Si profiles in the Arabian Sea are quite similar, except in the surface (Fig. 6.6a, b). Both of them increase with depth except in the surface where Nd concentrations are higher compared to subsurface indicating atmospheric/continental sources.

The concentration of silicon is almost zero near surface waters due to high productivity; gradually increases with depth and attains a maximum at a depth of about 2500 m and remains nearly constant in bottom waters (Fig. 6.6b). However, unlike Si, concentration of Nd is maximum in surface waters. The concentration of Nd is higher in the surface waters, gets removed and reaches minimum in the subsurface zone and gradually increases in deep and bottom waters. The overall results of Nd show significant linear correlation (r = 70) with the Si in the Arabian Sea water column (Fig. 6.7).



Fig. 6.6: The vertical profiles of dissolved (a) Nd and (b) Si in the Arabian Sea water column.



Fig. 6.7: The dissolved Nd vs. Si in the Arabian Sea water column.

The higher flux of Aeolian input, $1.5-13 \text{ g m}^2 \text{ y}^{-1}$, to the surface waters of the Arabian Sea could be responsible for the higher concentration of dissolved Nd in its surface waters (Sirocko and Sarnthein, 1989; Duce et al., 1991; Ramaswamy and Nair, 1994; Measures and Vink, 1999). In the subsurface region, Nd concentrations are depleted to minimum levels. The processes of adsorption and/or absorption of Nd through the colloidal and sinking particles can lead to their removal from the water column in the subsurface zone. Within the suboxic zone of the Arabian Sea, dissolved Nd concentrations enhance by about 10-25% as compared to the subsurface waters (Fig. 6.8a). The Nd concentrations obtained in the present study are within the range of previously reported values (German and Elderlield, 1990; Bertram and Elderfield, 1993; Goswami et al., 2014).



Fig. 6.8: The section plots for (a) Nd and (b) Nd isotopic composition in the Arabian Sea water column.
6.2.2 Nd isotopic compositions in the Arabian Sea waters

The results indicate large heterogeneity in the ε_{Nd} values of surface, intermediate and deeper waters of the Arabian Sea (Fig. 6.8b). ε_{Nd} in the water column of Arabian Sea varies from -14.4 to -5.6 (Table 6.1; Fig. 6.8b and 6.9). The less radiogenic ε_{Nd} values have been observed in the northern-most water column (Fig. 6.9c). The average uncertainty is 0.60 ε_{Nd} (2 σ). It is higher in a few of the samples due to the lower signal of Nd in mass spectrometer (Table 6.1). The observed ε_{Nd} in the present study are similar to those reported earlier in the South-Eastern Arabian Sea (Goswami et al., 2014).

 ε_{Nd} in surface waters of the South-Eastern Arabian Sea are less-radiogenic, -11.2 to -12.0 (Fig. 6.9a) and are similar to those observed in the surface waters of the BoB (Amakawa et al., 2000; Singh et al., 2012). It clearly indicates that the BoB surface waters enter into the surface Eastern Arabian Sea through the East Indian Coastal Currents (EICC). However, the surface waters in the central Arabian Sea are more radiogenic in ε_{Nd} (Fig. 6.9b and 6.10a) and Northern-most Arabian Sea waters have less radiogenic ε_{Nd} (Fig. 6.9c). Presently, the Aeolian dust deposition mass accumulation rates in the central and the eastern Arabian Sea are ~10-20 g m⁻² y⁻¹ and ~5-10 g m⁻² y⁻¹, respectively (Maher et al., 2010). The higher ε_{Nd} in the central Arabian Sea could originate from the mineral dust deposition emanating from the nearby landmasses. The surface and bottom waters of the Northern-most Arabian Sea are less-radiogenic in ε_{Nd} . This might be due to the supply of less radiogenic Nd from the dissolved/particulate phases of the Indus River. This inference is supported by the presence of the shelf sediments in the Indus fan with less-radiogenic ε_{Nd} (Clift et al., 2002). It can be surmised that the dissolution and/or leaching of particulates of the Indus, sinking and shelf sediments can supply less-radiogenic ε_{Nd} in the Northern Arabian Sea. The ε_{Nd} of the deep and bottom waters of the Arabian Sea are similar to NADW and AABW.





Fig. 6.9: The vertical patterns of Nd isotope composition in the water column of the (a) South-Eastern (b) Central and (c) Northern-most basins of the Arabian Sea (AS). The vertical profiles of ε_{Nd} in the AS show a North-South gradient with the Northern profiles exhibiting less radiogenic Nd compared to the later.

6.2.3 Quantification of the Arabian Sea water masses: inverse modeling approach

The dissolved Nd concentrations and its isotopic compositions present in the Arabian Sea waters is an end result of mixture of Nd contributed by a variety of water masses and its supply from atmospheric dust deposition, contribution of sinking particulates and/or from sediment at water - sediment interfaces. The contributions of Nd from different sources have been quantified following an 231 | P a g e inverse model approach (Goswami et al., 2014; Tarantola, 2005; Tripathy and Singh et al., 2012).

The use of inverse modeling in the present study is based on set of mass balance equations, which relates the experiential data with the model parameters. In this approach, the contributions of multiple sources (end-members) are approximated based on the experiential parameters. The inverse model quantifies the contribution of different sources to the observed quantity along with the optimum estimations of their end-members.

In the existing context, in order to find out the contribution of Nd from a variety of water masses (sources) in the water column of the Arabian Sea, the considered parameters are; (i) Salinity, (ii) Potential temperature, (iii) Nd concentration, and (iv) Nd isotopic composition (ϵ_{Nd}).

The mass balance equations are:

$$\left(\mathcal{E}_{Nd}\right)_{m} = \frac{\left(\mathcal{E}_{Nd}\right)_{m}^{excess} \times Nd_{m}^{excess} + \sum_{i=1}^{n} Nd_{i} \times \left(\mathcal{E}_{Nd}\right)_{i} \times f_{im}}{Nd_{m}^{excess} + \sum_{i=1}^{n} Nd_{i} \times f_{im}} \quad \dots \dots 6.4$$

232 | Page

where, f_{im} is the fraction of contribution by the ith water mass/source on the mth data point, Z is salinity and potential temperature of the water-mass (source/endmember), m is measured data of a sample or observation point, Nd_m^{excess} and $(\varepsilon_{Nd})_m^{excess}$ are excess Nd contribution with ε_{Nd} in the water column apart from the water masses considered in the present problem. The excess of Nd can come from the Aeolian dust or by the release from the sinking particles (Jeandel et al., 1995; Tachikawa et al., 1999; Singh et al., 2012; Goswami et al., 2014).

Data	θ (°C)	Salinity	Nd, pmol kg ⁻¹	ε _{Nd}
<u>a priori values</u>				
Rivers	28.00 ± 0.10	0.10 ± 0.10	6.60 ± 0.23	-15.70 ± 0.40
BoB	28.00 ± 0.20	30.00 ± 0.20	32.00 ± 1.12	-15.00 ± 0.40
ASHSW	26.80 ± 0.10	36.60 ± 0.10	10.90 ± 0.38	$\textbf{-7.10} \pm 0.40$
PGW	15.70 ± 0.10	35.90 ± 0.10	10.60 ± 0.37	-8.50 ± 0.40
RSW	10.50 ± 0.10	35.50 ± 0.10	12.20 ± 0.43	-9.40 ± 0.40
IW	13.50 ± 0.10	34.50 ± 0.10	11.60 ± 0.41	-2.90 ± 0.40
IIW	4.50 ± 0.10	34.60 ± 0.10	18.10 ± 0.63	-3.60 ± 0.40
NADW	1.80 ± 0.10	34.80 ± 0.10	19.90 ± 0.70	-10.50 ± 0.40
AABW	1.50 ± 0.10	34.70 ± 0.10	27.80 ± 0.97	$\textbf{-8.50} \pm 0.40$
a posterior val	ues			
Rivers	28.00 ± 0.10	0.13 ± 0.13	6.55 ± 0.23	-15.72 ± 0.40
BoB	31.39 ± 0.19	31.06 ± 0.20	27.06 ± 0.86	-14.22 ± 0.32
ASHSW	28.39 ± 0.09	37.34 ± 0.10	8.82 ± 0.26	$\textbf{-6.98} \pm 0.32$
PGW	15.65 ± 0.10	36.11 ± 0.10	9.69 ± 0.34	-8.52 ± 0.40
RSW	10.36 ± 0.10	36.08 ± 0.10	9.20 ± 0.28	-11.20 ± 0.39
IW	13.45 ± 0.10	34.65 ± 0.10	10.82 ± 0.38	-2.75 ± 0.38
IIW	4.38 ± 0.10	34.81 ± 0.10	16.45 ± 0.56	-3.23 ± 0.35
NADW	1.34 ± 0.07	35.22 ± 0.09	15.68 ± 0.48	-11.34 ± 0.35
AABW	0.76 ± 0.05	34.83 ± 0.07	2.94 ± 0.65	-8.51 ± 0.23

Table 6.2: The *a priori* and *a posterior* values of the various water masses end

 members used in the inverse model computations

In general, the above equations (6.3-6.6) can be written as d=F(m), where 'd' and 'm' are the data and model parameters respectively. F is the function that relates the data and model parameters. The model parameters are assumed to follow log-normal probability distribution. A non-linear weighted fit of equations (6.3-6.6) was obtained using the Quasi-Newton method (Tarantola, 2005), which provided the best possible set for the model parameters and the covariance (i.e. uncertainties) associated with them.

In the present study, a total of 9 water masses/sources (thus, n=9) have been considered. The details of these water masses have been given in the section 6.2.4.

6.2.4 *a priori* values of the end-members (source water masses)

The *a priori* values of various water masses are listed in Table 6.2, which are taken from the published literatures (Goswami et al., 2014). Nine number of water masses (sources/end-members; n=9; Table 6.2) have been considered in this study. The source/end-member properties (i.e., potential temperature, salinity, Nd concentration and ε_{Nd}) of these nine water masses are assumed to contribute to the potential temperature, salinity, dissolved Nd concentration and isotopic composition of waters of the region. These water masses/sources are, (i) Riverine supply to the Arabian Sea, (ii) Bay of Bengal (BoB) waters, (iii) Arabian Sea High Salinity Water (ASHSW), (iv) North Indian Intermediate Water (NIIW), (v) North Indian Deep Water (NIDW), (vi) Indonesian Through Flow surface Water (IW), (vii) Indonesian Through Flow Intermediate Water (IIW), (viii) Modified North Atlantic Deep Water (MNADW), and (ix) Antarctic Bottom Water (AABW).

6.2.5 *a posterior* values of the end-members (source water masses)

The inverse model derived *a posteriori* values of the various water masses end-members for potential temperature, salinity, Nd concentration and ε_{Nd} are listed in Table 6.2. The fractions of the different water masses (source) in the Arabian Sea determined from the inverse model are shown in Fig. 6.10.

6.2.6 The Arabian Sea water masses

The contributions of various water masses at the different depth profile estimated using inverse model are summarized below:

(i) **Riverine contribution**

The riverine contribution is almost negligible to the Arabian Seawater budget. The average river water (from the Indus and the west flowing rivers of India) contribution to the Arabian Sea water budget is ~2 (\pm 2.5) % with a range of 0.3-4.0 % which is a very small amount (Fig. 6.10, i).

(ii) Bay of Bengal contribution

The Bay of Bengal (BoB) waters contribute to the surface waters of the Arabian Sea (< 100 m; Fig. 6.10, ii). The contribution of BoB to the Eastern Arabian Sea shows a decreasing trend from south to north (Fig. 6.10, ii); with values decreasing from 50 (\pm 30) to 20 (\pm 10) %, the maximum value was found in the surface waters of the southernmost station SS 300/01. This is consistent with the known surface water circulation of this region (Goswami et al., 2014) during the sampling period when the EICC is active and transports BoB waters to the Arabian Sea around the southern tip of India.

(iii) Arabian Sea High Salinity Water

The Arabian Sea High Salinity Waters (ASHSW) originates in the Northern Arabian Sea due to excess evaporation and lower precipitation and gets transported towards the equator. The ASHSW is more dominant in top 200 m with a contribution of 80 (\pm 15) % in the Northern-most Arabian Sea and depletes to 50 (\pm 20) % towards the equator (Fig. 6.10, iii).



Fig. 6.10: The vertical distribution (in %) of various water masses in the Arabian Sea along the section (Figure 6.8): The riverine supply, BoB waters, ASHSW, NIIW, NIDW, IW, IIW, MNADW and AABW (i-ix). The numbers shown on the bottom of the graph indicate the station numbers.

(iv) The Persian Gulf and the Red Sea waters

Persian Gulf waters (PGW) originate in the Gulf of Persia with the high salinity and joins into the subsurface of the Arabian Sea waters through the Gulf of Oman. PGW contributes about 5 (\pm 10) to 15 (\pm 12) % to the Arabian Sea within the depth of 200 - 600 m. The PGW contribution gradually decreases from north to south (Fig. 6.10, iv). In addition, Red Sea waters (RSW) join into the Arabian Sea with high salinity and density at a depth range of about 200-1000 m. The RSW contribution varies from ~25 (\pm 15) to 80 (\pm 20) % to the Arabian Sea waters. The RSW contribution in the Arabian Sea also gradually depletes from north to south (Fig. 6.10, v).

(v) Indonesian Water and Indonesian Intermediate Water

The existences of Indonesian Water (IW) and Indonesian Intermediate Water (IIW) also have been observed in the Arabian Sea. The contribution of the IW and IIW to the Arabian Sea varies from $\sim 5 (\pm 3) - 20 (\pm 15) \%$ and $\sim 10 (\pm 8) - 10 (\pm 20) \%$ respectively (Fig. 6.10vi and vii). The contribution of IW and IIW behaves similarly to the BoB waters contribution, which depletes from south to north (Fig. 6.10, vi-vii).

(vi) Modified North Atlantic Deep and Antarctic Bottom waters

The deep and bottom waters present in the Arabian Sea are completely regulated by Modified North Atlantic Deep Water (MNADW) and Antarctic Bottom Water (AABW). The MNADW contributes about 25-80% with an average of 45 ± 15 % of water fraction to the Arabian Sea deep waters within the depth range of ~1000-2500 m depth (Fig. 6.10, viii). The AABW contributes a maximum of 75 ± 15 % water fraction to the Arabian Sea at a depth > 2500 m (Fig. 6.10, ix). These MNADW and AABW fractions in the Arabian Sea are similar to the previous studies in the Arabian Sea, BoB and the western Indian Ocean (Dileep Kumar and Li, 1996; Singh et al., 2012; Goswami et al., 2014).

Depth in (m)	Nd ^{excess}	Nd-err	ϵ_{Nd}^{excess}	ε _{Nd} -err
SS 300/01				
5	1.48	1.04	-6.05	1.99
170	1.20	2.28	-6.31	2.10
700	1.87	2.12	-5.65	1.87
1000	2.99	2.44	-6.15	2.01
1400	3.16	2.50	-6.15	2.01
1600	5.24	2.36	-7.40	2.23
1800	5.73	2.24	-8.32	2.29
2000	7.65	2.43	-6.82	1.82
2430	8.02	2.10	-11.15	2.31
SS 300/02				
3500	1.68	1.50	-6.08	1.99
4000	3.54	1.47	-5.70	1.78
SS 300/03				
2500	0.61	1.76	-5.87	1.95
3100	2.89	1.54	-5.47	1.78
SS 300/04				
5	1.12	1.06	-5.07	1.68
900	0.60	2.40	-6.01	2.00
1000	0.71	2.30	-5.94	1.98
2000	0.61	2.29	-5.94	1.98
2500	1.48	1.97	-6.03	2.00
3000	2.15	1.65	-6.30	2.04
4020	7.15	1.53	-7.04	1.79
SS 300/05				
5	0.06	0.86	-5.98	1.99
750	0.11	1.78	-5.95	1.98
1200	0.49	2.33	-6.00	2.00
3200	2.01	1.52	-5.78	1.87
4300	5.30	1.48	-6.34	1.85
SS 300/06				
80	1.26	1.06	-5.81	1.92
4125	3.27	1.49	-6.33	1.96
SS 300/07				
5	1.18	1.02	-10.26	1.67

Table 6.3: Excess Nd (Nd^{excess}, in pmol kg⁻¹) and their ε_{Nd} in the Arabian Seawaters computed using the inverse modeling of the data

238 | Page

1200	1.09	2.01	-12.05	2.00
3500	3.19	1.43	-12.26	1.97
3880	9.62	1.49	-11.44	1.48
SS 300/09				
5	1.65	1.03	-12.14	1.93
100	1.75	1.54	-13.33	2.15
200	1.44	1.75	-13.91	2.26
SS 300/10				
1800	0.15	1.28	-12.27	2.04

6.2.7 Estimates of Nd budget, Nd^{excess} and their ϵ_{Nd} { $(\epsilon_{Nd})^{excess}$ } from the inverse model

Using the analyzed and estimated values of Nd (from nine water masses), the excess value of Nd (Nd^{excess}) has been calculated for each sample (Table 6.3). The Nd^{excess} signifies the externally supplied Nd excluding the contribution from nine water masses. The Nd^{excess} over the Arabian Sea surface waters with a depth of ~5 to 100m, varies from 1.2 (\pm 1.0) to 1.75 (\pm 1.5) pmol kg⁻¹ with an average of ~1.4 \pm 1.1 pmol kg⁻¹ (Table 6.3; Fig. 6.11). Excess Nd computed in the surface water of the Arabian Sea accounts for 6 to 15% of the surface Nd budget. The northern most Arabian Sea (SS 300/09) water samples show high Nd^{excess} compared to the other surface waters. The estimated values of Nd^{excess} in the central Arabian Sea (SS 300/07) is $1.18 \pm 1.0 \text{ pmol kg}^{-1}$ (Table 6.3; Fig. 6.11a) which is almost 2.5 times lower compared to the previously reported Nd^{excess} near the location (0802; 14.42 °N, 69.42 °E) studied by Goswami et al. (2014). The average isotopic composition of the excess Nd $\{(\epsilon_{Nd})^{excess}\}$ in the Arabian Sea surface waters computed using inverse model is -7.55 ± 1.87 (Table 6.3; Fig. 6.11b). This is within the range of ε_{Nd} (= -6.0) supplied from dust over the Arabian Sea (Sirocko, 1995). It concludes that, the excess Nd in the Central Arabian Sea surface waters is supplied from dust deposition, which originates from the nearby landmasses. In addition to these surface waters, bottom waters

also exhibit extremely high Nd^{excess}. However, the excess Nd isotopic composition in the bottom waters varies from -5.7 to -12.3 indicating release of a large amount of Nd from the bottom sediments. The isotope composition of the excess Nd in the bottom waters of the South-Eastern Arabian Sea (SS 300/01) are less radiogenic, $(\epsilon_{Nd})^{excess}$ (= -11.2) compared to the other sections (Table 6.3; Fig. 6.21b). The upper most surface sediments from a nearby location in the South-Eastern Arabian Sea also show similar Nd isotopic composition of -9.4 whereas, Nd isotopic composition in the core-top sediments from the BoB is -15.5 (Tripathy et al., 2011; Goswami et al., 2014). The unradiogenic Nd^{excess} in the South-Eastern section of the Arabian Sea might be because of a significant release of Nd from G-B particles originated in the Himalayas. The BoB receives an annual supply of ~10¹² kg of riverine particles (Galy and France-Lanord, 2001; Unger et al., 2003) from these rivers. The ϵ_{Nd} of Nd^{excess} of the surface water in the South-Eastern Arabian Sea (SS 300/01) is -6.1 (± 2).

The Nd^{excess} in the Arabian Sea surface waters suggests its contribution from dust dissolution. The flux of dust deposition and rate of deposition can be estimated by approaching inverse model using the dissolved Nd in the surface waters. The Nd^{excess} in the surface waters can be used to estimate the dust flux over the Arabian Sea. The Nd^{excess} in the surface ocean waters is regulated by four parameters: the relative abundance of Nd in the Aeolian dust; fractional solubility of Nd in the surface ocean; depth of the mixed layer into which the dust is deposited and the residence time of Nd in the mixed layer of the ocean. Considering the values of the above parameters, the dust flux depositing over the ocean surface can be estimated using the eq. 6.5.

$$F_{dust} = \frac{Nd^{excess} \times M \times S \times \rho_{SW}}{f \times C_{Nd}} \times 100 \qquad \dots \dots 6.5$$

where, F_{dust} is the estimated dust flux upon the surface ocean (in g m⁻² y⁻¹), Nd^{excess} is the excess Nd (pg kg⁻¹) in the surface ocean; M is mixed layer depth in

meters; S is the scavenging factor which is 0.4 y^{-1} based upon a Nd residence time of 2.5 years in the surface ocean (Amakawa et al., 2000), ρ_{SW} is the density of seawater (in $g \text{ cm}^{-3}$), f is the solubility factor of Nd in the surface ocean originated from dust which is assumed to be 5%, similar to that of Al (Measures and Vink, 2000) and C_{Nd} is the Nd concentration in dust in $\mu g g^{-1}$. To estimate the dust flux over the Arabian Sea surface waters, the mixed layer depth in the Arabian Sea is taken to be 30m. The factor C_{Nd} i.e. the concentration of Nd in the dust was taken to be Nd concentration in the upper continental crust (26.5 μ g g⁻¹; Taylor and McLennan, 1995). The term Nd_{dust} in eq. 6.5 has been obtained by the Nd^{excess} in the Arabian Sea surface waters by the inverse model calculations (Table 6.3). By substituting all the parameters in eq. 6.5, the estimated dust flux varies from 1.50 to 2.20 g m⁻² y⁻¹ with an average of 1.8 ± 1.4 g m⁻² y⁻¹ over the Arabian Sea surface waters, which is relatively lower compared to the earlier reported dust deposition over the Arabian Sea 2.2-13 g m⁻² y⁻¹ (Sirocko and Sarntherin, 1989; Duce et al., 1991; Measures and Vink, 1999; Goswami et al., 2014). The estimate of lower dust deposition in the present study might be due to differences in seasonal dust deposition over the Arabian Sea.

The signature of high Nd^{excess} in the sub-oxic zone of the central Arabian Sea (SS 300/07; Fig. 6.11a) indicates the release of scavenged Nd from sinking particles in the oxygen minimum zone (OMZ). A similarity in the $\varepsilon_{Nd}^{excess}$ and those in the corresponding surface waters observed in the OMZ of the Arabian Sea indicate that the released Nd are sourced from corresponding surface waters. This implies that OMZ acts as a source of Nd and other redox trace elements in the sub-oxic ocean waters. The Nd^{excess} observed near in the bottom waters of the Arabian Sea (Fig. 6.11a, b) could be due to particle leaching at the water-sediment interface.



Fig. 6.11: The distribution of (a) excess Nd and (b) its corresponding ε_{Nd} in the Arabian Sea waters column quantified using the inverse model. The numbers shown on the bottom indicate the stations.

6.2.8 Hf concentrations and isotopic compositions in the Indian Ocean

The water samples have been collected from the Arabian Sea, the Bay of Bengal, the Andaman Sea and the Eastern Indian Ocean depth profiles during summer of 2012 and 2013, respectively, and analyzed for concentration of Hf and its isotopic compositions. The concentrations of Hf and ϵ_{Hf} in the analyzed water samples of the Arabian Sea and the Indian Ocean have been listed in Table 6.4.

6.2.8.1 Concentrations of dissolved Hf in the Indian Ocean

The analyzed concentrations of dissolved Hf in the Arabian Sea waters vary from 0.21 to 0.73 pmol kg⁻¹ (Table 6.4). The lowest concentrations of Hf have been observed in the subsurface of the southern Arabian Sea, whereas, the highest concentrations of Hf were found in the northern Arabian Sea surface waters near the shelf (Table 6.4). The Hf concentrations in the Arabian Sea waters along with the salinity, potential temperature and dissolved oxygen over the depth profiles have been plotted in Fig. 6.12 and 6.14a, respectively. Whereas, the overall concentration of Hf in the Indian Ocean vary from 0.21 to 1.27 pmol kg⁻¹, and have been plotted as a function of depth (Fig. 6.13). The distribution patterns of concentrations of Hf in the Indian Ocean depth profiles are shown in Fig. 6.15a.

Table 6.4: Salinity, potential temperature (θ) , concentration of Hf and its isotope composition in the Arabian Sea, the Andaman Sea, the Bay of Bengal, and the Eastern Indian Ocean water column

Depth (m)	Salinity	θ , °C	Hf, pmol kg ⁻¹	ε _{Hf}	$\pm \sigma \epsilon_{Hf}$			
Arabian Sea								
<u>SS 300/01 (9.43 °N; 75.15 °E)</u>								
5	34.51	29.9	-	-2.06	0.40			
<u>SS 300/03 (3.00 °N; 6</u>	<u>SS 300/03 (3.00 °N; 68.10 °E)</u>							
5	34.95	29.66	0.21	-	-			
200	35.34	19.81	0.37	-	-			
750	35.12	8.71	0.37	-6.82	1.07			
1300	34.91	5.40	0.41	-	-			
2500	34.76	1.99	0.51	-1.10	1.44			
3470	34.74	1.41	0.67	0.17	0.74			
<u>SS 300/05 (11.00 °N;</u>	<u>68.00 °E)</u>							
5	34.97	29.8	0.42	-10.74	0.58			
100	36.28	26.13	0.21	-7.96	0.76			
620	35.41	10.95	0.45	-	-			
1200	35.09	6.62	0.66	-2.16	0.29			
2100	34.81	2.62	0.52	0.41	0.70			
3200	34.74	1.49	0.73	-	-			
<u>SS 300/09 (19.00 °N; 67.98 °E)</u>								

5	36.53	28.87	0.36	-8.38	0.41		
290	35.87	14.60	0.35	-	-		
600	35.67	11.69	0.51	-	-		
1000	35.38	8.48	-	1.37	0.92		
1500	35.04	5.14	0.54	-	-		
3200	34.75	1.52	-	2.14	0.68		
	А	ndaman Se	a				
SK 304 – 16 (0833 °N	SK 304 – 16 (0833 °N: 95.00 °E)						
15	32.17	30.05	0.27	-0.04	0.93		
<u>SK 304 – 17 (11.00 °N</u>	N; 95.00 °E)						
10	32.14	31.01	0.36	-5.15	1.65		
100	34.38	21.33	0.27	-	-		
300	34.77	12.9	0.41	-3.52	1.61		
600	34.83	9.32	0.4	3.89	1.91		
800	34.79	8.05	0.48	4.05	0.78		
1000	34.75	6.68	0.53	7.78	0.33		
1600	34.70	4.98	0.49	4.39	0.34		
2200	34.69	4.79	0.61	4.58	0.27		
2800	34.69	4.76	0.55	5.87	0.40		
3350	34.68	4.76	0.57	4.34	0.28		
	В	ay of Benga	al				
<u>SK 304 – 21 (13.50 °N</u>	N; 91.00 °E)						
10	34.56	30.67	0.41	-10.35	0.35		
100	34.74	22.65	0.24	-3.72	0.34		
300	34.79	11.43	0.38	5.71	0.37		
600	34.64	8 07					
0.7.7	2.110.1	0.97	0.56	4.01	0.31		
800	34.55	7.86	0.56 0.48	4.01 5.54	0.31 0.21		
800 1000	34.55 34.03	7.86 6.51	0.56 0.48 0.38	4.01 5.54 6.30	0.31 0.21 0.27		
800 1000 1500	34.55 34.03 32.65	7.86 6.51 4.41	0.56 0.48 0.38 0.52	4.01 5.54 6.30 4.61	0.31 0.21 0.27 0.29		
800 1000 1500 2000	34.55 34.03 32.65 32.05	7.86 6.51 4.41 2.62	0.56 0.48 0.38 0.52 0.59	4.01 5.54 6.30 4.61 -3.31	0.31 0.21 0.27 0.29 0.24		
800 1000 1500 2000 2400	34.55 34.03 32.65 32.05 31.64	7.86 6.51 4.41 2.62 2.05	0.56 0.48 0.38 0.52 0.59 0.68	4.01 5.54 6.30 4.61 -3.31 -3.28	0.31 0.21 0.27 0.29 0.24 0.18		
800 1000 1500 2000 2400 2850	34.55 34.03 32.65 32.05 31.64 31.67	7.86 6.51 4.41 2.62 2.05 1.58	0.56 0.48 0.38 0.52 0.59 0.68 0.57	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49	0.31 0.21 0.27 0.29 0.24 0.18 0.22		
800 1000 1500 2000 2400 2850	34.55 34.03 32.65 32.05 31.64 31.67	7.86 6.51 4.41 2.62 2.05 1.58 ndian Ocea	0.56 0.48 0.38 0.52 0.59 0.68 0.57 n	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49	0.31 0.21 0.27 0.29 0.24 0.18 0.22		
800 1000 1500 2000 2400 2850 SK 304 – 06 (0.53 °S;	34.55 34.03 32.65 32.05 31.64 31.67 In 86.56 °E)	7.86 6.51 4.41 2.62 2.05 1.58 ndian Ocea	0.56 0.48 0.38 0.52 0.59 0.68 0.57 n	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49	0.31 0.21 0.27 0.29 0.24 0.18 0.22		
800 1000 1500 2000 2400 2850 <u>SK 304 – 06 (0.53 °S;</u> 10	34.55 34.03 32.65 32.05 31.64 31.67 In 86.56 °E) 34.37	7.86 6.51 4.41 2.62 2.05 1.58 ndian Ocea	0.56 0.48 0.38 0.52 0.59 0.68 0.57 n 0.22	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49 1.43	0.31 0.21 0.27 0.29 0.24 0.18 0.22 1.97		
800 1000 1500 2000 2400 2850 <u>SK 304 – 06 (0.53 °S;</u> 10 100	34.55 34.03 32.65 32.05 31.64 31.67 In 86.56 °E) 34.37 35.27	7.86 6.51 4.41 2.62 2.05 1.58 ndian Ocea 29.91 19.96	0.56 0.48 0.38 0.52 0.59 0.68 0.57 n 0.22 0.30	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49 1.43	0.31 0.21 0.27 0.29 0.24 0.18 0.22 1.97 -		
800 1000 1500 2000 2400 2850 <u>SK 304 – 06 (0.53 °S;</u> 10 100 300	34.55 34.03 32.65 32.05 31.64 31.67 B6.56 °E) 34.37 35.27 35.06	7.86 6.51 4.41 2.62 2.05 1.58 ndian Ocea 29.91 19.96 11.64	0.56 0.48 0.38 0.52 0.59 0.68 0.57 n 0.22 0.30 0.45	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49 1.43 - -1.44	0.31 0.21 0.27 0.29 0.24 0.18 0.22 1.97 - 0.91		
800 1000 1500 2000 2400 2850 SK 304 – 06 (0.53 °S; 10 100 300 600	34.55 34.03 32.65 32.05 31.64 31.67 b 86.56 °E) 34.37 35.27 35.06 35.00	7.86 6.51 4.41 2.62 2.05 1.58 ndian Ocea 29.91 19.96 11.64 9.47	0.56 0.48 0.38 0.52 0.59 0.68 0.57 n 0.22 0.30 0.45 0.49	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49 1.43 - -1.44 3.09	0.31 0.21 0.27 0.29 0.24 0.18 0.22 1.97 - 0.91 0.44		
800 1000 1500 2000 2400 2850 <u>SK 304 – 06 (0.53 °S;</u> 10 100 300 600 1000	34.55 34.03 32.65 32.05 31.64 31.67 B6.56 °E) 34.37 35.27 35.06 35.00 34.95	7.86 6.51 4.41 2.62 2.05 1.58 ndian Ocea 29.91 19.96 11.64 9.47 6.88	0.56 0.48 0.38 0.52 0.59 0.68 0.57 n 0.22 0.30 0.45 0.49 0.52	4.01 5.54 6.30 4.61 -3.31 -3.28 -2.49 1.43 - 1.43 - 1.44 3.09 2.23	0.31 0.21 0.27 0.29 0.24 0.18 0.22 1.97 - 0.91 0.44 0.52		

244 | Page

2500	34 74	1.82	0.73	4 96	0.48			
3500	34.74	1.02	1.27	4.20	0.40			
4550	34.72	1.19	0.82	3 95	0.77			
550 54.72 1.04 0.82 5.95 $0.59SK 304 - 08 (11 16 °S; 08 00 °F)$								
7	34.26	29.15	0.25	1.14	0.88			
50	35.48	27.13	0.23	1.14	0.00			
100	34.63	27.75	0.32	7 / 1	1 77			
300	34.85	10.96	0.55	1.67	0.52			
500 600	34.05	7.68	0.57	2.88	0.32			
1000	34.75	7.00	0.53	2.00	0.87			
1000 SK 304 - 10 (16 02 °S	54.70 5• 104 46 °F)	0.55	1.99	0.28			
10	34 29	2 28 48	0.26	-7 95	0.96			
100	34.62	20.40	0.20	-2 55	0.90			
250	35.67	16.06	0.30	-5.09	0.78			
500	34.66	8.71	0.34	-	-			
1000	34.69	4.97	0.66	2.37	0.92			
1800	34.75	2.71	0.72	2.54	0.42			
2700	34.77	1.62	0.83	1.80	1.03			
3700	34.76	1.02	0.94	0.23	0.36			
4700	34.74	0.78	0.60	-0.56	0.32			
5700	34.74	0.70	0.91	0.64	0.32			
<u>SK 304 - 11 (06.50 °S</u>	5; 97.66 °E)							
5	33.80	29.5	0.47	-4.55	1.06			
<u>SK 304 – 13 (01.76 °S</u>	5; 94.37 °E)							
10	34.13	29.98	0.33	-6.40	0.72			
100	34.80	25.25	0.25	0.13	0.77			
300	34.93	12.1	0.34	-2.57	0.33			
600	34.85	9.31	0.36	2.50	0.41			
800	34.84	7.67	0.39	0.10	0.30			
1000	34.82	6.75	0.23	5.35	0.38			
1500	34.71	3.99	0.45	-0.94	0.35			
2500	34.44	1.83	0.77	3.23	0.35			
3500	34.63	1.11	0.62	2.83	0.30			
4650	34.63	0.8	0.68	2.86	0.19			
<u>SK 304 – 14 (03.24 °N; 92.93 °E)</u>								
5	34.08	30	0.26	-6.12	0.66			

-: Not Analyzed, Hf and ε_{Hf} are analyzed in limited samples only due to the requirement of large volume samples (~60-100 L).



Fig. 6.12: The vertical distribution patterns of the Hf concentration and its isotope composition along with the variations of salinity and potential temperature in the Arabian Sea.

The higher concentration of Hf in the surface waters of the Northern Arabian Sea (SS 300/05 and 09; Fig. 6. 12) could be due to the interaction of water with particles coming from Aeolian dust, shelf and fluvial sediments originating from the nearby land masses. Subsurface waters of the Arabian Sea are characterized by lower Hf contents resulting from their removal from the water column by adsorption and/or absorption on the sinking lithogenic/biological particles. The concentration of Hf in the intermediate and deep waters of the Arabian Sea increases with depth due to the re-mineralization of the scavenged particles. The concentrations of Hf in the Arabian Sea profiles are similar to those observed for the nutrients except in the surface waters (Fig. 6.12).



Fig. 6.13: The vertical distribution patterns of the Hf concentrations and its isotope compositions in the water column of the Eastern Indian Ocean, the Andaman Sea and the Bay of Bengal along with the variations in salinity and potential temperature for six stations SK 304/06, 08, 10, 13, 17 and 21.

Below suboxic zone, the dissolved concentration of Hf in the Arabian Sea increases to a maximum (Fig. 6.12 and 6.14a). The increased concentrations of Hf similar to the Nd values, below suboxic zone might be a consequence of remineralization of scavenged particles. Towards the sea/sediment interface, dissolved Hf concentrations are systematically lower in the Arabian Sea. Concentrations of Hf are lowest in the shallow waters above 200 m (0.21-0.47 pmol kg⁻¹; Fig. 6.13 and 15a). They increase gradually to a maximum (0.21-1.27 pmol kg⁻¹) at a depth of ~3500 m corresponding to the Atlantic and Antarctic Ocean waters, and then they moderately deplete (0.57-0.91 pmol kg⁻¹) towards the sea/sediment interface (Fig. 6.13 and 14a). The Hf concentrations in the Andaman Sea (SK304/17) and BoB (SK304/21) water profiles display lower values (Fig. 6.15a). The lower concentration of Hf values in the BoB and the Andaman basins could be due to the high freshwater input with low concentration levels from the Himalayan River systems such as the G-B, Irrawaddy and the Salween and dilution by intense precipitation. Adsorption of Hf on the large quantity of sediments delivered by the Ganga-Brahmaputra and the Irrawaddy and Salween in the BoB and the Andaman Sea respectively could be another reason for its lower concentration. Moderately higher concentrations of Hf are obtained in the deep waters of eastern most station (SK304/10) compared to the other sections in the Indian Ocean.

However, concentration of Hf in intermediate and deeper waters in all the stations are high compared to their surface waters (Fig. 6.14, 15a). It could be due to the re-mineralization of scavenged Hf from sinking particles in the intermediate and deeper waters. The depleted concentrations of Hf in bottom-most waters could be due to the re-adsorption of dissolved Hf onto the clay particles near water-sediment interface. In general, overall Hf concentrations in the Indian Ocean are bracketed between the Atlantic and the Pacific Ocean waters (Rickli et al., 2009, 2010, 2014; Zimmermann et al., 2009a, b; Stichel et al., 2012).



Fig. 6.14: The distribution patterns of (a) the concentration of Hf and (b) the Hf isotope compositions in the water column of the Arabian Sea.

6.2.8.2 Hf isotopic compositions in the Indian Ocean water masses

This section describes the variability observed in Hf isotope composition in water column of the Indian Ocean and possible reason for these variabilities. The internal precision of the Hf isotope composition is about 0.6 ϵ unit (2 σ) in most of the samples except few of the surface samples. In a few surface samples, it is ~3 ϵ unit (2 σ , Table 6.4) owing to their lower Hf concentration. The overall Hf isotope compositions in water column of the Arabian Sea display large variability, $\epsilon_{\rm Hf} = -10.74 (\pm 0.58)$ to +2.14 (± 0.68) (Table 6.4; Fig. 6.12 and 6.14b). The results indicate large heterogeneity in the ε_{Hf} values of surface, intermediate and deeper waters of the Arabian Sea (Fig. 6.12, 14b). The $\varepsilon_{\rm Hf}$ values in the Arabian Sea surface waters vary from -10.74 to -2.06 and are quite unradiogenic; however, intermediate and deeper waters are comparatively more radiogenic, ranging from -7.96 (\pm 0.96) to +2.14 (\pm 0.68). Further, the surface waters of the Northern (SS300_09) Arabian Sea are having less radiogenic Hf compared to that of the South-Eastern Arabian Sea surface waters (SS300/01; Fig. 6.12). The values of ε_{Hf} in the subsurface and intermediate waters of the Arabian Sea vary from -7.96 to +1.37 (± 0.92). The heterogeneity of ε_{Hf} values in the Arabian Sea waters indicates the existence of a variety of water masses and its regulation by different sources within the basin. However, from the surface towards deep to bottom, ε_{Hf} gets more radiogenic. The similar behavior was observed in deep and bottom waters of the Atlantic, Antarctic, Arctic and the Pacific Ocean depth profiles (Rickli et al., 2009, 2010; Zimmermann et al., 2009a, b). Non-radiogenic Hf in the surface waters of the Arabian Sea could result from its supply from the leaching from Aeolian dust emanating from the nearby land masses, as has been observed in case of Nd. Hf isotope composition of the dust depositing over the Arabian Sea are not available, however, ε_{Hf} of the Sahara/Sahel region indicates large variability (-20 to -0.6, Rickli et al., 2009). This needs to be confirmed by measuring Hf isotope composition of the dust pouring over the Arabian Sea.

The variation and distribution patterns of dissolved Hf isotopic compositions present in the BoB, the Andaman Sea and the Eastern Indian Ocean have been plotted as a function of depth (Fig. 6.13 and 6.15b). Surface water of the Bay of Bengal (SK304 - 21) has quite less radiogenic Hf, which is possibly resulting from the dissolution of non-radiogenic Hf from the sediments delivered from the G-B system. Bed-load and suspended sediments of the G-B in Bangladesh have $\varepsilon_{\rm Hf}$ ranging from -30.2 to -18.3 (Garcon et al., 2013). Similarly



Fig. 6.15: The distribution patterns of (a) concentration of Hf and (b) ϵ_{Hf} in the Indian Ocean water column along with the sampling locations.

the non-radiogenic Hf, albeit with large uncertainty, of the surface waters of the Andaman Sea (SK304 – 17) could also be derived from sediments of the Irrawaddy and the Salween. Overall, the dissolved ε_{Hf} in the Indian Ocean varies with a wide range of -10.4 to +7.8 (Table 6.4). ε_{Hf} varies from -5.0 to +7.8 and - 3.3 to +5.9 in the intermediate and deeper waters towards the water - sediment interface respectively (Table 6.4; Fig. 6.13).



Fig. 6.16: The vertical distribution of Hf isotopic compositions in the water column of (a) the Arabian Sea, the Andaman Sea and the Bay of Bengal and (b) the Eastern Indian Ocean along with the dissolved ε_{Hf} data reported in the other global oceans. The global data are compiled from Godfrey et al., (2009), Rickli et al., (2009, 2014), and Zimmermann et al., (2009a, b).

The ε_{Hf} in the Andaman Sea vertical profiles (SK 304B – 16 and 17) vary from -5.15 to +7.78 (Fig. 6.16a). However, the southernmost surface waters of the Andaman Sea has more radiogenic ε_{Hf} , -0.04 (± 0.93), which could be due to the input of high radiogenic Pacific waters through the Malacca Strait or it could be due to local volcanic input. The subsurface and deeper waters of the Andaman Sea have highly radiogenic ε_{Hf} , which could be due to the volcanic inputs.

In the BoB, ε_{Hf} varies with a large range of -10.35 in the surface to +6.30 in the intermediate waters (Fig. 6.16a). The ε_{Hf} varies from -10.35 to -3.72, +4.0 to +6.30 and -3.31 to -2.49 in the surface, intermediate and deep to bottom waters respectively. The BoB seems to be quite a unique basin in which the surface and deep to bottom waters are having unradiogenic ε_{Hf} with radiogenic Hf in the intermediate waters. The intermediate waters of the BoB with more radiogenic Hf are similar to those of the Andaman Sea. This indicates the supply of the Intermediate water from the Andaman Sea to the Eastern Bay of Bengal. As discussed in the case of surface waters of the BoB, non-radiogenic Hf signatures of the deep/bottom waters of the Bay of Bengal are derived from the sediments of the G-B origin (Garçon et al., 2013).

The ε_{Hf} in the surface waters of the Eastern Indian Ocean vary with an immense range of -7.95 to +7.41. The Eastern-most Indian Ocean surface waters analyzed in this study is un-radiogenic compared to the other surface waters. This could be due to the Aeolian dust and/or erosion of continents from nearby land-masses. This results need to be conformed to more measurements. ε_{Hf} in the surface waters of the Southern Indian Ocean (SK304 – 6,8,9) are more radiogenic, which could be due to the significant contribution of Pacific waters entering through ITF with high radiogenic ε_{Hf} (= +5.7 ± 1.4; Zimmermann et al., 2009a)... The deep and bottom waters from the Indian Ocean display ranges of 0.32 - 4.96 and -0.56 - +3.95, respectively, close to the NADW (ε_{Hf} = +3.2; Rickli et al., 2009) and AABW (ε_{Hf} = +4.4; Rickli et al., 2014) reported in the Atlantic Ocean.

These results (Fig. 6.16b) indicate that, the NADW and AABW regulate the deep and bottom waters in the Indian Ocean. However, the Hf isotope compositions of these waters get modified locally due to the supply of non-radiogenic Hf from the sediments derived locally in the ocean basin or delivered through the large rivers such the Indus, the Ganga-Brahmaputra, and the Irrawaddy-Salween systems.

It is interesting to note that ε_{Hf} in the surface waters of the Indian Ocean are least radiogenic among all Hf isotope data of the different oceans reported till date (Fig. 6.16a). Despite large uncertainties observed in Hf isotope data of some of the surface waters, this observation is confirmed in the Bay of Bengal surface waters with ε_{Hf} , -10.35 ± 0.35. The particulates from the Himalayan Rivers such as the Indus, G-B, Irrawaddy and the Salween, and bottom sediments of the Northern Indian Ocean contribute less radiogenic ε_{Nd} to the northern Indian Ocean waters (Singh et al., 2012; Goswami et al., 2014 and this study). Due to the similar nature of Nd and Hf, the particulates from the Himalayan Rivers and Aeolian dust could be the source of un-radiogenic ε_{Hf} in the Arabian Sea and other Indian Ocean surface and shallow waters (Fig. 6.16b; Godfrey et al., 1997; Vervoort et al., 1999; van de Flierdt et al., 2002, 2004a, b, 2006, 2016; Rickli et al., 2010, Garçon et al., 2013). The deep and bottom waters of the Indian Ocean have more radiogenic ε_{Hf} similar or marginally lower compared to the deep and bottom waters of the Atlantic, Antarctic, and the Pacific Ocean.

6.3 Conclusions

Release of Nd from particles modifies dissolved Nd isotope budget of the Arabian Sea. ε_{Nd} of surface waters of the central and southern Arabian Sea gets radiogenic Nd from dust particles originating from nearby landmasses. Northern Arabian Sea water gets less radiogenic Nd from sediments of Indus River. Surface waters present in the South-Eastern Arabian Sea receive a significant contribution

from the BoB. Using the inverse model derived excess Nd in the surface waters, the estimated dust flux over the Arabian Sea is 1.8 ± 1.4 g m⁻² y⁻¹.

The Arabian Sea is described with several water masses. The Arabian Sea high salinity waters, Persian Gulf waters, Red Sea waters, Indonesian Waters and Bay of Bengal surface waters are present in the surface to 1000 m depth in the water column with a fraction of 70, 12, 45, 10 and 35%, respectively. At depth of ~1000 to 2500m, Indonesian Intermediate waters contribute 15% waters. However, the deep and bottom waters in the Arabian Sea are composed of the North Atlantic deep waters and Antarctic Bottom waters with a maximum contribution of 45 and 75%, respectively.

Continental input through the silicate weathering acts as a major controller of the dissolved ε_{Hf} in the surface waters of the Arabian Sea. However, along with the MNADW and AABW circulations, leaching of particulates regulate the dissolved ε_{Hf} in the deep and bottom waters of the Arabian Sea.

The surface waters of the North-Eastern Indian Ocean receive significant dissolved chemical flux from the Himalayan Rivers such as the G-B, Indus, Irrawaddy and the Salween and peninsular Indian rivers namely the Godavari, Mahanadi and the Narmada etc. However, the Australian and African Rivers regulate the dissolved chemical flux of the surface waters in the Eastern Indian Ocean. The Hf isotopic compositions in the deep and bottom waters in the Indian Ocean are within the range of the Atlantic, Antarctic, and the Pacific Ocean waters. NADW and AABW circulations regulate the deep and bottom water masses in the Indian Ocean. The Indian Ocean. The Indian Ocean. The intermediate water masses in the Eastern Indian Ocean are controlled by the ITF waters and Antarctica circumpolar currents.

Chapter 7

Conclusions and future perspectives

The primary objectives of this thesis, as mentioned in Chapter-1 are to study (i) the chemical weathering, associated CO₂ consumption and fluxes of trace elements and isotopes from the river systems draining the Peninsular India and their impact on the global carbon and oceanic trace elements budgets, (ii) behavior of trace elements and isotopes in the East Indian Estuaries determining their source/sink nature and their influence on the global marine budgets of trace elements, nutrients and micronutrients, (iii) sources of sediments and factors influencing the provenance, dispersal and deposition of sediments in the shelf region with special reference to the Andaman Shelf (iv) the water masses present in the Arabian Sea and in the Eastern Indian Ocean using Nd and Hf isotopes and quantifying the budgets of these isotopes in the Northern Indian Ocean and studying the factors impacting these budgets such as the ocean circulations, riverine input, boundary exchange, desorption from particulates and atmospheric dust deposition. The above objectives have been addressed by studying the spatial and temporal variations in the major, trace elements and isotope composition in the natural waters and sediments of the respective rivers, estuaries and the Indian Ocean. Dissolved Nd and Hf isotope compositions have been analyzed in the Arabian Sea and the Indian Ocean water column to construct their possible sources and water masses. Chemical separation and measurement protocols of Hf isotopes have been established in our laboratory for the first time as a part of this thesis. The major outcomes of this study have been summarized below.

7.1 Chemical erosion in the Peninsular Indian rivers and associated chemical fluxes to the Bay of Bengal

This study indicates that the Godavari, Mahanadi and the Brahmani Rivers, three important rivers of the Peninsular India debouch into the Bay of Bengal with an average TDS flux of 20, 4 and 0.75 MT y⁻¹, respectively. In the Godavari River system, Na⁺ and HCO₃⁻ were the most abundant cation and anion in most of the samples followed by Ca⁺² and Cl⁻, respectively, whereas, in the Mahanadi and the Brahmani Ca⁺² and HCO₃⁻ were the dominant cation and anion in all the samples followed by Na⁺ and Cl⁻, indicating their contribution from chemical weathering along with precipitation, dissolution of saline/alkaline soils and anthropogenic inputs. The up-stream waters of the GRS are higher in TDS compared to the downstream waters.

Inverse model based estimates in the Godavari and forward model estimates in the Mahanadi and the Brahmani Rivers display variable erosion rates in these river basins. The silicate erosion rates in the Godavari, Mahanadi and the Brahmani Rivers vary between 4.0-22.8, 4.9-11.3 and 6.5-10.4 tons km⁻² y⁻¹ respectively; whereas, the carbonate weathering rates in them display a range of 3-50, 8.1-51.5 and 9.1-14.6 tons km⁻² y⁻¹, respectively. The corresponding CO₂ consumption rates resulting from the silicate weathering in the Godavari, Mahanadi and the Brahmani River basins vary within the range of (1.2-9.0, 0.7-2.1 and 0.8-1.4) × 10⁵ mol km⁻² y⁻¹. The total CO₂ draw-down due to the silicate weathering in the Godavari, Mahanadi and the Brahmani River basins are about (5.23, 1.8 and 0.3) × 10¹⁰ mol y⁻¹, respectively, which account for ~0.60, 0.21 and 0.033% of the annual global CO₂ consumption (870 × 10¹⁰ mol y⁻¹) due to silicate weathering.

The chemical weathering in the Godavari, Mahanadi and the Brahmani Rivers delivers the dissolved Sr flux of 124, 22 and 3.6 million moles per annum to the BoB with ⁸⁷Sr/⁸⁶Sr ratio of 0.714642, 0.728543 and 0.731144, respectively. The dissolved ε_{Nd} in the GRS displays spatial and temporal variations between - 5.2 and -32.8 reflecting the drained lithology. The head-waters of the GRS draining the Deccan Trap basalts are more radiogenic in ε_{Nd} as compared to the downstream waters, which mostly flow through the Archeans. The chemical weathering in the Godavari River, annually delivers 11.8×10^3 moles of dissolved Nd to the BoB with ε_{Nd} of -22.8.

The ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ and ε_{Nd} in particulate matters of the GRS varies from 0.708634 to 0.949058 and -4.0 to -37.5, respectively. The sediments collected in the higher reached of the GRS eroding the Deccan basalts are more radiogenic in ε_{Nd} (-4 to -10.6) and less radiogenic in ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ (0.708634 to 0.714111) whereas,

the sediments in the lower basin draining the Achaean cratons posses high radiogenic 87 Sr/ 86 Sr (0.730678 to 0.949058) and less radiogenic ε_{Nd} (-15 to -37.5). The results of 87 Sr/ 86 Sr and ε_{Nd} in sediments existing in the GRS suggest that, the sediments discharged into the BoB are mixture of three sources viz. the Deccan Trap basalts, eastern and western Dharwar cratons and eastern gneisses. Silicate weathering contributes little to the dissolved Sr budget of the GRS, whereas dissolved ε_{Nd} budget the GRS is dominantly controlled by weathering of silicate minerals. Finally, GRS delivers 22.6 and 0.6 M kg y⁻¹ of particulate Sr and Nd flux into the BoB annually with 87 Sr/ 86 Sr and ε_{Nd} of 0.755278 and -27.5, respectively.

Finally, this study observed that lithology is the primary factor controlling the chemical weathering, and weathering rate of basalt is faster compared to that of gneisses. After lithology, runoff seems to have the dominant control on silicate erosion rate in the peninsular India. The Godavari, Mahanadi and the Brahmani Rivers sequester ~0.84% of atmospheric CO_2 from 0.86% of global exhore area impacting global climate on million years' timescale.

7.2 Behavior of trace elements and isotopes in solute and particles of the Eastern Indian Estuaries: Implications to their global marine budget

In this study, the Sr concentrations and its isotope composition (⁸⁷Sr/⁸⁶Sr) were determined in dissolved and particulate phases in the Ganga (Hooghly), the Godavari and the Krishna estuaries connected to the Bay of Bengal. The results clearly indicated that, submarine groundwater discharge (SGD) is an important source of trace elements and isotopes to the ocean and regulates the oceanic budgets of dissolved chemical compositions like nutrients, trace elements and isotopes along with the riverine and aeolian dust deposition. Inverse model based material balance calculations using concentration of Sr, ⁸⁷Sr/⁸⁶Sr ratio and salinity of these estuaries show SGD as an additional important source that contributes water flux to the ocean, ~0.5-50 % of riverine discharge during monsoon. The average SGD flow rate, during monsoon, in the G-B, Krishna and the Godavari

estuaries are 5545, 155 and 1735 m³ s⁻¹ respectively. These SGD flow rates annually supplies (660, 59.4 and 58.7) × 10⁶ moles of Sr to the G-B, Krishna and the Godavari estuaries, respectively and hence to the Bay of Bengal. The overall Sr flux through the SGD from the East Indian estuaries is 7.8×10^8 mole y⁻¹ which is ~3-11% of the worldwide SGD Sr flux (0.7-2.8 × 10¹⁰ mole y⁻¹) with annual average seepage of 0.75×10^4 m³ s⁻¹ which is about 2-10% of the global SGD (7.5-35 × 10⁴ m³ s⁻¹; Beck et al., 2013). This study underscores the application of Sr concentration and its isotopic composition to quantify the flux of submarine groundwater discharge to the estuaries and coastal regions.

Further, my study in these estuaries on REEs, Mn and Nd isotopes in dissolved and particulate phases reveals two distinct processes operating in the East Indian estuaries; viz, removal of dissolved trace metals (e.g. REEs, Mn) in the low salinity zones due to the salt – induced coagulation of river colloids and their release in mid-high salinity zones due to re-dissolution or desorption of Fe-Mn hydroxides. The hydrographical and morphological properties of estuaries play a key role in removal and/or release of trace elements in the mixing zones. The fractionation of dissolved REEs leads to change in their relative abundances in the ocean. In these estuaries, sub-oxic zone operate as a principal controlling parameter of dissolved REE and Mn. Re-dissolution of Fe-Mn hydroxides behaves as a foci source in release of dissolved trace elements (REEs, Fe-Mn, and lighter Mo etc.). The estuarine sediments release huge amount of selected trace metals and act as considerable sources of the dissolved TEIs to the ocean. Fractionation in the REE patterns is observed during both removal and release processes. The SPM dissolution and SGD also can contribute to the excess dissolved REEs in the mixing zones. The East Indian estuaries are the potential sources of dissolved Nd, ~260 Mg per year, which could be very significant to the missing Nd budget and also to other trace elements' budgets in the modern global Ocean.

7.3 Lithology, monsoon and sea surface current control on provenance, dispersal and deposition of sediments over the Andaman continental shelf

Major element and Sr and Nd concentrations and their isotope composition have been determined in the silicate fraction of the sediments deposited on the Northern and the Eastern Andaman Shelf to constrain their sources and factors influencing their erosion, dispersal, and deposition. Major element composition of the majority of these sediments indicates their ferromagnesian nature which is sourced from mafic lithologies present in the drainage of the Irrawaddy River and over the IBA. Sr and Nd isotope compositions of the Andaman Shelf sediments suggest that these sediments are mostly derived from (i) the Irrawaddy River, (ii) the Salween River, (iii) the IBA ranges either through the smaller rivers flowing through the Arakan coast or through the Irrawaddy River whose western tributaries such as the Chindwin etc are draining these ranges and (iv) the Western/Central granitic belts of the Myanmar and Thailand through the Tavoy, the Tanintharyi and other smaller rivers. The erosion and sediment delivery from these sources are controlled by the intense and focussed precipitation over the high relief on the western slopes of these ranges and further dispersed by the eastward sea-surface current controlled by SW monsoon on the Northern and the Eastern shelf of the Andaman Sea. This study for the first time recognises the higher erosion rates on the western slopes of the granitic ranges of the Southern Myanmar, supplying significant amount of sediment to the Eastern Andaman Shelf around the Mergui Archipelago.

7.4 Dissolved ε_{Nd} and ε_{Hf} in the Indian Ocean waters: Implications to water-particle interaction, upwelling, water mass mixing and their sources

Concentration of Nd and its isotope composition have been determined in the water columns along $69^{\circ}E$ meridional sections in the Arabian Sea to track and quantify various water masses and various sources impacting the Nd budget in this basin.

The Arabian Sea consists of several water masses which were identified and quantified using Nd isotope composition of the water masses. The Arabian Sea high salinity waters, Persian Gulf waters, Red Sea waters and the Bay of Bengal surface waters are present in the surface to 1000 m depth of water columns in the Arabian Sea with a fraction of 85, 20, 60 and 50%, respectively. River water contribution to the surface water is insignificant. The Indonesian waters and the Indonesian Intermediate waters contribute ~20 to 25% in the depth range of ~1000 to 2500 m. The deep and bottom waters in the Arabian Sea are composed of the North Atlantic deep waters and Antarctic Bottom waters with a maximum contribution of 65 and 85%, respectively.

The Nd isotope budget is largely controlled by the different water masses present in the Arabian Sea. In addition, a significant amount of Nd is added to the water column of the Arabian Sea from the dissolution of particles of Aeolian and the riverine origin and from shelf and bottom sediments. Waters of the northern Arabian Sea get less radiogenic Nd from sediments supplied by the Indus River. Surface waters of the central and the southern Arabian Sea get more radiogenic Nd from dust particles originating from nearby landmasses. Average dust flux, 1.8 \pm 1.4 g m⁻² y⁻¹ over the Arabian Sea has been estimated in this thesis based on the excess Nd present in the surface waters of the Arabian Sea using inverse model and the Nd concentration in the dust particles.

Further, Hf isotope composition of waters of the Arabian Sea and the eastern Indian Ocean has been used for the first time to identify the water masses present in these basins. For this application, chemical separation and measurement protocols have been developed successfully in our laboratory to determine the concentrations of Hf and its isotope composition in dissolved phase. The external precision of the measurements of concentration and isotope compositions are ~7% and $0.4\pm0.2 \epsilon_{Hf}$ and depend on its concentration in the water column.

Distribution of Hf isotopic compositions in the deep and bottom waters in the Indian Ocean is within the range of Atlantic, Antarctic and Pacific Ocean waters. The results emphasize that, the ε_{Hf} in the surface waters of the Arabian Sea is controlled by nearby continental input through the silicate weathering, whereas, the ε_{Hf} variations in the deep and bottom waters are regulated by NADW and AABW. It indicates that, the deep and bottom water masses in the Indian Ocean are regulated by NADW and AABWs. The Southern intermediate waters in the Indian Ocean seem to be controlled by the Indonesian through flow waters (ITF) and the Antarctica circumpolar currents. The details of distribution patterns of ε_{Hf} in the Indian Ocean waters need to be understood by studying its possible sources.

7.5 Future perspectives

Research carried out in this thesis highlights a detailed study of the physical and chemical weathering of a few major peninsular Indian rivers, behaviour of trace elements and isotopes in the East Indian estuaries, concentration and isotopic composition of Nd and Hf, assessment of water masses in the Indian Ocean, and the factors influencing the deposition of shelf sediments and their dispersal patterns in the Andaman Basin. The outcomes of this research lead to a few interesting scientific problems which need to be studied in future. A brief description is as follows:

(i) The current study of weathering and flux estimates from the Peninsular basins of India is based on snapshot sampling during monsoon. Though it represents the majority of the flux, to assess the dominant controlling factor on the erosion and weathering in the peninsular basin, study should be carried out with seasonal sampling along with measurements of rainfall, water flux, and temperature. This will also provide the precise flux of trace elements and isotopes from these basins to the bay of Bengal. The role of saline/alkaline soils, anthropogenic activity should be evaluated in the small scale catchments.

(ii) Temporal variation in the fluxes of various trace elements and isotopes including the nutrients and micronutrients should be evaluated in the various estuaries, particularly the role of particles in contributing to the disolved fluxes. These are important as the particle concentration in the estuaries display large seasonal variabilities. In addition, temporal variation in the paleo-river water and groundwater discharges on the time scale of tens to hundreds of thousand years

can be traced using the Sr isotopes in the forams preserved the sediments of these estuaries.

(iii) Sr and Nd isotope composition of sediments from the Andaman shelf shows significant spatial variations. The deposition and dispersal of sediments in the Andaman Basin are influenced by the factors such as monsoon and surface currents etc. Very little is known about the weathering and erosion in hinterland the Irrawaddy, Salween and other river basins of Myanmar. Erosion distribution in these basins should be determined which enables researchers to know the sources of sediments, dissolved material to the Andaman Sea and the factors influencing the erosion patterns.

(iv) This research work presents important results on concentration and isotope composition of Hf for the first time, along with that of Nd in the Indian Ocean water columns. The combination of the Hf-Nd isotope composition endorses various sources and their contribution to the water masses in the Indian Ocean. A detailed study of Hf-Nd concentration and their isotope composition in the water column of the Indian Ocean is required to study circulation patterns of the surface (warm path), intermediate (IIW), deep (NADW) and bottom waters (AABW). Further, with knowledge of contemporary water masses present in the Indian Ocean, Nd isotope composition preserved in the forams of the sediments deposited in these basin could be used to study the temporal variation of Indonesian Through Flow and Tethyan waters which impacted the monsoon climate of the globe on different time scales.

REFERENCES

- Acharyya, S.K., Gupta, A., and Orihashi, Y. (2008). U–Pb zircon dates (LA-ICP-MS) of some felsic magmatic rocks from the basal parts of the Dhanjori basin and their stratigraphic implication, East Singhbhum, India. IAGR Conference Series 5, 151–152.
- Ahmad, S.M., Anil Babu, G., Padmakumari, V.M., Dayal, A.M., Sukhija, B.S., and Nagabhushanam, P. (2005). Sr, Nd isotopic evidence of terrigenous flux variations in the Bay of Bengal: Implications of monsoons during the last ~34,000 years. Geophysical Research Letters 32, n/a-n/a.
- Ahmad, S.M., Padmakumari, V.M., and Anil Babu, G. (2009). Strontium and neodymium isotopic compositions in sediments from Godavari, Krishna and Pennar rivers. Current Science 97, 1766-1769.
- Alagarsamy, R., You, C.-F., Nath, B.N., and Sijin Kumar A.V. (2010). Determination of rare earth, major and trace elements in authigenic fraction of Andaman Sea (Northeastern Indian Ocean). sediments by Inductively Coupled Plasma-Mass Spectrometry. Microchemical Journal 94, 90-97.
- Albarède, F., Simonetti, A., Vervoort, J.D., Blichert-Toft, J., and Abouchami, W. (1998). A Hf-Nd isotopic correlation in ferromanganese nodules. Geophysical Research Letters 25, 3895-3898.
- Ali, S., Hathorne, E.C., Frank, M., Gebregiorgis, D., Stattegger, K., Stumpf, R., Kutterolf, S., Johnson, J.E., and Giosan, L. (2015). South Asian monsoon history over the past 60 kyr recorded by radiogenic isotopes and clay mineral assemblages in the Andaman Sea. Geochemistry, Geophysics, Geosystems 16, 505-521.
- Allègre, C.J., Louvat, P., Gaillardet, J., Meynadier, L., Rad, S., and Capmas, F. (2010). The fundamental role of island arc weathering in the oceanic Sr isotope budget. Earth and Planetary Science Letters 292, 51-56.
- ALLEN, R., NAJMAN, Y., CARTER, A., BARFOD, D., BICKLE, M.J., CHAPMAN, H.J., GARZANTI, E., VEZZOLI, G., ANDÒ, S., and PARRISH, R.R. (2008). Provenance of the Tertiary sedimentary rocks of the Indo-Burman Ranges, Burma (Myanmar): Burman arc or Himalayanderived? Journal of the Geological Society 165, 1045-1057.
- Altabet, M.A., Higginson, M.J., and Murray, D.W. (2002). The effect of millennial-scale changes in Arabian Sea denitrification on atmospheric CO₂. Nature 415, 159-162.
- Amakawa, H., Alibo, D.S., and Nozaki, Y. (2000). Nd isotopic composition and REE pattern in the surface waters of the eastern Indian Ocean and its adjacent seas. Geochimica et Cosmochimica Acta 64, 1715-1727.
- Amakawa, H., Nozaki, Y., Alibo, D.S., Zhang, J., Fukugawa, K., and Nagai, H. (2004). Neodymium isotopic variations in Northwest Pacific waters. Geochimica et Cosmochimica Acta 68, 715-727.
- Amiotte Suchet., and Probst, J. -L. (1995). A global model for present-day atmospheric/soil CO₂ consumption by chemical erosion of continental rocks. Tellus, 273-280.
- Amiotte Suchet, P., Probst, J.-L., and Ludwig, W. (2003). Worldwide distribution of continental rock lithology: Implications for the atmospheric/soil CO₂ uptake by continental weathering and alkalinity river transport to the oceans. Global Biogeochemical Cycles 17, n/a-n/a.
- Arsouze, T., Dutay, J., Lacan, F., and Jeandel, C. (2009). Reconstructing the Nd oceanic cycle using a coupled dynamical-biogeochemical model. Biogeosciences 6, 2829-2846.

- Åström, M. E., Österholm, P., Gustafsson, J. P., Nystrand, M., Peltola, P., Nordmyr L., and Boman A. (2012). Attenuation of rare earth elements in a boreal estuary. Geochimica et Cosmochimica Acta 96, 105-119.
- Audry, S., Blanc, G., Schäfer, J., Chaillou, G., and Robert, S. (2006). Early diagenesis of trace metals (Cd, Cu, Co, Ni, U, Mo, and V). in the freshwater reaches of a macrotidal estuary. Geochimica et Cosmochimica Acta 70, 2264-2282.
- Audry, S., Blanc, G., Schäfer, J., Guérin, F., Masson, M., and Robert, S. (2007). Budgets of Mn, Cd and Cu in the macrotidal Gironde estuary (SW France). Marine Chemistry 107, 433-448.
- Awasthi, N., Ray, J.S., Singh, A.K., Band, S.T., and Rai, V.K. (2014). Provenance of the Late Quaternary sediments in the Andaman Sea: Implications for monsoon variability and ocean circulation. Geochemistry, Geophysics, Geosystems 15, 3890-3906.
- Banner, J.L. (2004). Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy. Earth-Science Reviews 65, 141-194.
- Barrat, J.A., and Nesbitt, R.W., 1996. Geochemistry of the Tertiary volcanism of Northern Ireland. Chemical Geology 129, 15-38.
- Basu, A.R., Jacobsen, S.B., Poreda, R.J., Dowling, C.B., and Aggarwal, P.K. (2001). Large Groundwater Strontium Flux to the Oceans from the Bengal Basin and the Marine Strontium Isotope Record. Science 293, 1470-1473.
- Beck, A.J., Charette, M.A., Cochran, J.K., Gonneea, M.E., and Peucker-Ehrenbrink, B. (2013). Dissolved strontium in the subterranean estuary-Implications for the marine strontium isotope budget. Geochimica et Cosmochimica Acta 117, 33-52.

- Berner, E.K., and Berner, R.A. (1996). Global environment: water. Air, and Geochemical Cycles: Prentice Hall, New York.
- Berner, E.K., and Berner, R.A. (2012). Global environment: water, air, and geochemical cycles. Princeton University Press.
- Berner, R.A., Lasaga, A.C., and Garrels, R.M. (1983). The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years. American Journal of Science 283, 641-683.
- Bertram, C.J., and Elderfield, H. (1993). The geochemical balance of the rare earth elements and neodymium isotopes in the oceans. Geochimica et Cosmochimica Acta 57, 1957-1986.
- Bhanumati, R., and Ray, A. (2000). Design and development of an information system and creation of constituent databases for the organised storage of available isotope age data on Indian rocks, part V (Lesser Himalayas, pp. 1-14)., part VI (Higher Himalayas, pp. 1-15). and part VII (Trans-Himalayas, pp. 1-14)., all with data sheets. Geochronology and Isotope Geology Div., Geological Survey of India, Calcutta (unpublished).
- Bhaskar Rao, Y.J., Sivaraman, T.V., Pantulu, G.V.C., Gopalan, K., and Naqvi,
 S.M. (1992). Rb-Sr ages of late Archean metavolcanics and granites,
 Dharwar craton, South India and evidence for Early Proterozoic thermotectonic event (s). Precambrian Research 59, 145-170.
- Bickle, M.J., Bunbury, J., Chapman, H.J., Harris, N.B., Fairchild, I.J., and Ahmad, T. (2003). Fluxes of Sr into the headwaters of the Ganges. Geochimica et Cosmochimica Acta 67, 2567-2584.
- Bickle, M.J., Chapman, H.J., Bunbury, J., Harris, N.B., Fairchild, I.J., Ahmad, T., and Pomiès, C. (2005). Relative contributions of silicate and carbonate rocks to riverine Sr fluxes in the headwaters of the Ganges. Geochimica et Cosmochimica Acta 69, 2221-2240.

- Bickle, M.J., Harris, N.B.W., Bunbury, J.M., Chapman, H.J., Fairchild, I.J., and Ahmad, T. (2001). Controls on the 87Sr/86Sr Ratio of Carbonates in the Garhwal Himalaya, Headwaters of the Ganges. Journal of Geology 109, 737-753.
- Bikshamaiah, G., and Subramanian, V. (1980). Chemical and sediment mass transfer in the Godavari River basin in India. Journal of Hydrology 46, 331-342.
- Biksham, G., and Subramanian, V. (1988a). Elemental composition of Godavari sediments (central and southern Indian subcontinent). Chemical Geology 70, 275-286.
- Biksham, G., and Subramanian, V. (1988b). Nature of solute transport in the Godavari Basin, India. Journal of Hydrology 103, 375-392.
- Biksham, G., and Subramanian, V. (1988c). Sediment transport of the Godavari River Basin and its controlling factors. Journal of Hydrology 101, 275-290.
- Biksham, G., Subramanian, V., Ramanathan, A., and Van Grieken, R. (1991). Heavy metal distribution in the Godavari river basin. Environmental Geology and Water Sciences 17, 117-126.
- Biller, D.V., and Bruland, K.W. (2012). Analysis of Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in seawater using the Nobias-chelate PA1 resin and magnetic sector inductively coupled plasma mass spectrometry (ICP-MS). Marine Chemistry 130-131, 12-20.
- Bird, M.I., Robinson, R.A.J., Win Oo, N., Maung Aye, M., Lu, X.X., Higgitt, D.L., Swe, A., Tun, T., Lhaing Win, S., Sandar Aye, K., Mi Mi Win, K., and Hoey, T.B. (2008). A preliminary estimate of organic carbon transport by the Ayeyarwady (Irrawaddy). and Thanlwin (Salween). Rivers of Myanmar. Quaternary International 186, 113-122.

- Blum, J.D., and Erel, Y. (1997). Rb-Sr isotope systematics of a granitic soil chronosequence: The importance of biotite weathering. Geochimica et Cosmochimica Acta 61, 3193-3204.
- BLUTH, G.J.S., and KUMP, L.R. (1994). Lithologic and climatologic controls of river chemistry. Geochimica et Cosmochimica Acta 58, 2341-2359.
- Bouquillon, A., France-Lanord, C., Michard, A., and Tiercelin, J.-J. (1987). SEDIMENTOLOGY AND ISOTOPIC CHEMISTRY OF THE BENGAL FAN SEDIMENTS: THE DENUDATION OF THE HIMALAYA1, 5, Proceedings of the Ocean Drilling Program: Scientific Results. The Program, p. 43.
- Bouquillon, A., France-Lanord, C., Michard, A., and Tiercelin, J. J. (1990). Sedimentology and isotopic chemistry of the Bengal fan sediments: the denudation of the Himalaya. Proc. Ocean Drill. Prog. Sci. Results. 116, 43 – 58.
- Boyle, E.A., Bergquist, B.A., Kayser, R.A., and Mahowald, N. (2005). Iron, manganese, and lead at Hawaii Ocean Time-series station ALOHA:
 Temporal variability and an intermediate water hydrothermal plume.
 Geochimica et Cosmochimica Acta 69, 933-952.
- Boyle, E., Collier, R., Dengler, A.T., Edmond, J.M., Ng, A.C., and Stallard, R.F. (1974). On the chemical mass-balance in estuaries. Geochimica et Cosmochimica Acta 38, 1719-1728.
- Boyle, E.A., Edmond, J.M., and Sholkovitz, E.R. (1977). The mechanism of iron removal in estuaries. Geochimica et Cosmochimica Acta 41, 1313-1324.
- Brass, G.W. (1976). The variation of the marine 87Sr86Sr ratio during Phanerozonic time: interpretation using a flux model. Geochimica et Cosmochimica Acta 40, 721-730.

- Broecker, W. (1963). Radioisotopes and large-scale oceanic mixing. The sea 2, 88-108.
- Broecker, W.S. (1991). The great ocean conveyor. Oceanography 4, 79-89.
- Bruland, K.W., Donut, J.R., and Hutchins, D.A. (1991). Interactive influences of bioactive trace metals on biological production in oceanic waters. Limnol. Oceanogr 36, 1555-1577.
- Burke, W., Denison, R., Hetherington, E., Koepnick, R., Nelson, H., and Otto, J. (1982). Variation of seawater ⁸⁷Sr/⁸⁶Sr throughout Phanerozoic time. Geology 10, 516-519.
- Burnett, B., Chanton, J., Christoff, J., Kontar, E., Krupa, S., Lambert, M., Moore,
 W., O'Rourke, D., Paulsen, R., and Smith, C. (2002). Assessing methodologies for measuring groundwater discharge to the ocean. Eos, Transactions American Geophysical Union 83, 117-123.
- Burnett, W., Bokuniewicz, H., Huettel, M., Moore, W., and Taniguchi, M. (2003). Groundwater and pore water inputs to the coastal zone. Biogeochemistry 66, 3-33.
- Burnett, W.C., Aggarwal, P.K., Aureli, A., Bokuniewicz, H., Cable, J.E., Charette, M.A., Kontar, E., Krupa, S., Kulkarni, K.M., Loveless, A., Moore, W.S., Oberdorfer, J.A., Oliveira, J., Ozyurt, N., Povinec, P., Privitera, A.M.G., Rajar, R., Ramessur, R.T., Scholten, J., Stieglitz, T., Taniguchi, M., and Turner, J.V. (2006). Quantifying submarine groundwater discharge in the coastal zone via multiple methods. Science of The Total Environment 367, 498-543.
- Calvert, S.E. and Pedersen, T.F. (1993). Geochemistry of Recent oxic and anoxic marine sediments: Implications for the geological record. Marine Geology 113, 67-88.
- Chaki, A., Shivkumar, K., and Dey, S. (2008). Geochemistry and Rb-Sr geochronology of granitoids from northern parts of Bastar Craton, central

India: implications to petrogenesis and geodynamics. Mem. Geol. Soc. India 73, 101-116.

- Chakrapani, G., and Subramanian, V. (1990). Preliminary studies on the geochemistry of the Mahanadi river basin, India. Chemical Geology 81, 241-253.
- Chakrapani, G.J., and Subramanian, V. (1993). Conventry Groundwater Investigation: Sources and Movement of Chlorinated Hydrocarbon Solvents Rates of erosion and sedimentation in the Mahanadi river basin, India. Journal of Hydrology 149, 39-48.
- Chandrasekharam, D., Mahoney, J.J., Sheth, H.C., and Duncan, R.A. (1999). Elemental and Nd-Sr-Pb isotope geochemistry of flows and dikes from the Tapi rift, Deccan flood basalt province, India. Journal of Volcanology and Geothermal Research 93, 111-123.
- Chapman, H., Bickle, M., Thaw, S.H., and Thiam, H.N. (2015). Chemical fluxes from time series sampling of the Irrawaddy and Salween Rivers, Myanmar. Chemical Geology 401, 15-27.
- Charette, M.A., and Sholkovitz, E.R. (2006). Trace element cycling in a subterranean estuary: Part 2. Geochemistry of the pore water. Geochimica et Cosmochimica Acta 70, 811-826.
- Chatterjee, J. (2013). Isotopic and Geochemical Studies of Saline-Alkaline soils, Water and Sediments of the Ganga river system: Implications to Erosion and Carbon cycle, Department of Geology. Mohanlal Sukhadia University, Udiapur (Raj).
- Chaturvedi, M.C. (2012). Ganga-Brahmaputra-Meghna Waters. CRC Press, pp. 1-450.
- Church, T.M. (1996). An underground route for the water cycle. Nature 380, 579-580.

- Church, T.M., Sarin, M.M., Fleisher, M.Q., and Ferdelman, T.G. (1996). Salt marshes: An important coastal sink for dissolved uranium. Geochimica et Cosmochimica Acta 60, 3879-3887.
- Clift, P.D., Lee, J.I., Hildebrand, P., Shimizu, N., Layne, G.D., Blusztajn, J., Blum, J.D., Garzanti, E., and Khan, A.A. (2002). Nd and Pb isotope variability in the Indus River System: implications for sediment provenance and crustal heterogeneity in the Western Himalaya. Earth and Planetary Science Letters 200, 91-106.
- Coale, K.H. (1991). Effects of iron, manganese, copper, and zinc enrichments on productivity and biomass in the subarctic Pacific. Limnology and Oceanography 36, 1851-1864.
- Colin, C., Turpin, L., Bertaux, J., Desprairies, A., and Kissel, C. (1999). Erosional history of the Himalayan and Burman ranges during the last two glacialinterglacial cycles. Earth and Planetary Science Letters 171, 647-660.
- Colin, C., Turpin, L., Blamart, D., Frank, N., Kissel, C., and Duchamp, S. (2006).
 Evolution of weathering patterns in the Indo-Burman Ranges over the last 280 kyr: Effects of sediment provenance on ⁸⁷Sr/⁸⁶Sr ratios tracer. Geochemistry, Geophysics, Geosystems 7, n/a-n/a.
- Conway, T.M., and John, S.G. (2014). Quantification of dissolved iron sources to the North Atlantic Ocean. Nature 511, 212-215.
- Coonley, L.S., Baker, E.B., and Holland, H.D. (1971). Iron in the Mullica River and in Great Bay, New Jersey. Chemical Geology 7, 51-63.
- Dalai, T., Krishnaswami, S., and Sarin, M. (2002). Major ion chemistry in the headwaters of the Yamuna river system:: Chemical weathering, its temperature dependence and CO₂ consumption in the Himalaya. Geochimica et Cosmochimica Acta 66, 3397-3416.

- Dalai, T.K., Krishnaswami, S., and Kumar, A. (2003). Sr and ⁸⁷Sr/⁸⁶Sr in the Yamuna River System in the Himalaya: sources, fluxes, and controls on Sr isotope composition. Geochimica et Cosmochimica Acta 67, 2931-2948.
- Damodararao, K., Singh, S.K., Rai, V.K., Ramaswamy, V., and Rao, P.S. (2016). Lithology, monsoon and sea-surface current control on provenance, dispersal and deposition of sediments over the Andaman continental shelf. Frontiers in Marine Science 3.
- Darbyshire, D., and Swainbank, I. (1988). South-east Asia Granite Project: Geochronology of a Selection of Granites from Burma.
- Das, A., and Krishnaswami, S. (2007). Elemental geochemistry of river sediments from the Deccan Traps, India: implications to sources of elements and their mobility during basalt-water interaction. Chemical Geology 242, 232-254.
- Das, A., Krishnaswami, S., and Kumar, A. (2006). Sr and ⁸⁷Sr/⁸⁶Sr in rivers draining the Deccan Traps (India).: Implications to weathering, Sr fluxes, and the marine ⁸⁷Sr/⁸⁶Sr record around K/T. Geochemistry, Geophysics, Geosystems 7, n/a-n/a.
- Das, A., Krishnaswami, S., Sarin, M., and Pande, K. (2005). Chemical weathering in the Krishna Basin and Western Ghats of the Deccan Traps, India: Rates of basalt weathering and their controls. Geochimica et Cosmochimica Acta 69, 2067-2084.
- Das, A., Pawar, N.J., and Veizer, J. (2011). Sources of sulfur in Deccan Trap rivers: A reconnaissance isotope study. Applied Geochemistry 26, 301-307.
- David, K., Frank, M., O'Nions, R.K., Belshaw, N.S., and Arden, J.W. (2001). The Hf isotope composition of global seawater and the evolution of Hf

isotopes in the deep Pacific Ocean from Fe-Mn crusts. Chemical Geology 178, 23-42.

- Davis, A.C., Bickle, M.J., and Teagle, D.A.H. (2003). Imbalance in the oceanic strontium budget. Earth and Planetary Science Letters 211, 173-187.
- De, S., Mazumder, R., Ohta, T., Hegner, E., Yamada, K., Bhattacharyya, T., Chiarenzelli, J., Altermann, W., and Arima, M. (2015). Geochemical and Sm-Nd isotopic characteristics of the Late Archaean-Palaeoproterozoic Dhanjori and Chaibasa metasedimentary rocks, Singhbhum craton, E. India: Implications for provenance, and contemporary basin tectonics. Precambrian Research 256, 62-78.
- De Villiers, S. (1999). Seawater strontium and Sr/Ca variability in the Atlantic and Pacific oceans. Earth and Planetary Science Letters 171, 623-634.
- DePaolo, D.J., and Ingram, B.L. (1985). High-resolution stratigraphy with strontium isotopes. Science 227, 938-941.
- Dessert, C., Dupré, B., François, L.M., Schott, J., Gaillardet, J., Chakrapani, G., and Bajpai, S. (2001). Erosion of Deccan Traps determined by river geochemistry: impact on the global climate and the ⁸⁷Sr/⁸⁶Sr ratio of seawater. Earth and Planetary Science Letters 188, 459-474.
- Dessert, C., Dupré, B., Gaillardet, J., François, L.M., and Allegre, C.J. (2003). Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. Chemical Geology 202, 257-273.
- Dileep Kumar, M. and Li, Y.-H. (1996). Spreading of water masses and regeneration of silica and ²²⁶Ra in the Indian Ocean. Deep Sea Research Part II: Topical Studies in Oceanography 43, 83-110.
- Drever, J.I., (2005). Surface and Ground Water, Weathering, and Soils: Treatise on Geochemistry. Elsevier.

- Drever, J.I. and Smith, C.L. (1978). Cyclic wetting and drying of the soil zone as an influence on the chemistry of ground water in arid terrains. American Journal of Science 278, 1448-1454.
- Duce, R., Liss, P., Merrill, J., Atlas, E., Buat-Menard, P., Hicks, B., Miller, J., Prospero, J., Arimoto, R., and Church, T. (1991). The atmospheric input of trace species to the world ocean. Global biogeochemical cycles 5, 193-259.
- Dwivedi, A.K., Pandey, U.K., Murugan, C., Bhatt, A.K., Ramesh Babu, P.V., and Joshi, M. (2011). Geochemistry and geochronology of A-type Barabazar granite: Implications on the geodynamics of South Purulia Shear Zone, Singhbhum craton, Eastern India. Journal of the Geological Society of India 77, 527-538.
- Eckert, J.M., and Sholkovitz, E.R. (1976). The flocculation of iron, aluminium and humates from river water by electrolytes. Geochimica et Cosmochimica Acta 40, 847-848.
- Edmond, J. (1992). Himalayan tectonics, weathering processes, and the strontium isotope record in marine limestones. SCIENCE-NEW YORK THEN WASHINGTON- 258, 1594-1594.
- Edmond, J.M., and Huh, Y. (1997). Chemical weathering yields from basement and orogenic terrains in hot and cold climates, Tectonic uplift and climate change. Springer, pp. 329-351.
- Elderfield, H. (1986). Strontium isotope stratigraphy. Palaeogeography, Palaeoclimatology, Palaeoecology 57, 71-90.
- Elderfield, H., and Greaves, M.J. (1982). The rare earth elements in seawater. Nature 296, 214-219.
- Elderfield, H., Upstill-Goddard, R., and Sholkovitz, E.R. (1990). The rare earth elements in rivers, estuaries, and coastal seas and their significance to the

composition of ocean waters. Geochimica et Cosmochimica Acta 54, 971-991.

- Eriksson, P.G., Mazumder, R., Catuneanu, O., Bumby, A.J., and Ilondo, B.O. (2006). Precambrian continental freeboard and geological evolution: a time perspective. Earth-Science Reviews 79, 165–204.
- Faure, G. (1977). Principles of isotope geology.
- France-Lanord, C., and Derry, L.A. (1997). Organic carbon burial forcing of the carbon cycle from Himalayan erosion. Nature 390, 65-67.
- France-Lanord, C., Derry, L., and Michard, A. (1993). Evolution of the Himalaya since Miocene time: isotopic and sedimentological evidence from the Bengal Fan. Geological Society, London, Special Publications 74, 603-621.
- Frank, M. (2002). Radiogenic Isotopes: Tracers of past ocean circulation and erosional input. Reviews of Geophysics 40, 1-1-1-38.
- Gaillardet, J., Dupre, B., Allegre, C.J., and Négrel, P. (1997). Chemical and physical denudation in the Amazon River Basin. Chemical Geology 142, 141-173.
- Gaillardet, J., Dupré, B., Louvat, P., and Allègre, C.J. (1999). Global silicate weathering and CO₂ consumption rates deduced from the chemistry of large rivers. Chemical Geology 159, 3-30.
- Galy, A., and France-Lanord, C. (1999). Weathering processes in the Ganges-Brahmaputra basin and the riverine alkalinity budget. Chemical Geology 159, 31-60.
- Galy, A. and France-Lanord, C. (2001). Higher erosion rates in the Himalaya: Geochemical constraints on riverine fluxes. Geology 29, 23-26.
- Galy, A., France-Lanord, C., and Derry, L.A. (1996). The Late Oligocene-Early Miocene Himalayan belt Constraints deduced from isotopic compositions

of Early Miocene turbidites in the Bengal Fan. Tectonophysics 260, 109-118.

- Galy, A., France-Lanord, C., and Derry, L.A. (1999). The strontium isotopic budget of Himalayan rivers in Nepal and Bangladesh. Geochimica et Cosmochimica Acta 63, 1905-1925.
- Galy, V., France-Lanord, C., Peucker-Ehrenbrink, B., and Huyghe, P. (2010). Sr-Nd-Os evidence for a stable erosion regime in the Himalaya during the past 12 Myr. Earth and Planetary Science Letters 290, 474-480.
- Garcia-Orellana, J., Cochran, J., Bokuniewicz, H., Daniel, J., Rodellas, V., and Heilbrun, C. (2014). Evaluation of 224 Ra as a tracer for submarine groundwater discharge in Long Island Sound (NY). Geochimica et Cosmochimica Acta 141, 314-330.
- Garcia-Orellana, J., Rodellas, V., Casacuberta, N., Lopez-Castillo, E., Vilarrasa, M., Moreno, V., Garcia-Solsona, E., and Masqué, P. (2013). Submarine groundwater discharge: Natural radioactivity accumulation in a wetland ecosystem. Marine Chemistry 156, 61-72.
- Garçon, M., Chauvel, C., France-Lanord, C., Huyghe, P., and Lavé, J. (2013). Continental sedimentary processes decouple Nd and Hf isotopes. Geochimica et Cosmochimica Acta 121, 177-195.
- Garzanti, E., Vezzoli, G., Andò, S., Paparella, P., and Clift, P.D. (2005). Petrology of Indus River sands: a key to interpret erosion history of the Western Himalayan Syntaxis. Earth and Planetary Science Letters 229, 287-302.
- German, C.R., Casciotti, K.A., Dutay, J.-C., Heimbürger, L.E., Jenkins, W.J., Measures, C.I., Mills, R.A., Obata, H., Schlitzer, R., Tagliabue, A., Turner, D.R., and Whitby, H. (2016). Hydrothermal impacts on trace element and isotope ocean biogeochemistry. Philosophical Transactions of

the Royal Society A: Mathematical, Physical and Engineering Sciences 374.

- German, C.R. and Elderfield, H. (1990). Rare earth elements in the NW Indian Ocean. Geochimica et Cosmochimica Acta 54, 1929-1940.
- Glé, C., Del Amo, Y., Sautour, B., Laborde, P., and Chardy, P. (2008). Variability of nutrients and phytoplankton primary production in a shallow macrotidal coastal ecosystem (Arcachon Bay, France). Estuarine, Coastal and Shelf Science 76, 642-656.
- Godfrey, L.V., Lee, D.C., Sangrey, W.F., Halliday, A.N., Salters, V.J.M., Hein, J.R., and White, W.M. (1997). The Hf isotopic composition of ferromanganese nodules and crusts and hydrothermal manganese deposits: Implications for seawater Hf. Earth and Planetary Science Letters 151, 91-105.
- Godfrey, L.V., Zimmermann, B., Lee, D.C., King, R.L., Vervoort, J.D., Sherrell,R.M., and Halliday, A.N. (2009). Hafnium and neodymium isotope variations in NE Atlantic seawater. Geochemistry, Geophysics, Geosystems 10, n/a-n/a.
- Goldstein, S.J., and Jacobsen, S.B. (1987). The Nd and Sr isotopic systematics of river-water dissolved material: Implications for the sources of Nd and Sr in seawater. Chemical Geology: Isotope Geoscience section 66, 245-272.
- Goldstein, S.J., and Jacobsen, S.B., (1988a). Nd and Sr isotopic systematics of river water suspended material: implications for crustal evolution. Earth and Planetary Science Letters 87, 249-265.
- Goldstein, S.J., and Jacobsen, S.B. (1988b). Rare earth elements in river waters. Earth and Planetary Science Letters 89, 35-47.

- Goldstein, S.J., and Jacobsen, S.B., (1988c). REE in the Great Whale River estuary, northwest Quebec. Earth and Planetary Science Letters 88, 241-252.
- Goldstein, S.L., and Hemming, S.R. (2003). 6.17 Long-lived Isotopic Tracers in Oceanography, Paleoceanography, and Ice-sheet Dynamics, in: Holland, H.D., Turekian, K.K. (Eds.)., Treatise on Geochemistry. Pergamon, Oxford, pp. 453-489.
- Goldstein, S.L., and O'Nions, R.K. (1981). Nd and Sr isotopic relationships in pelagic clays and ferromanganese deposits. Nature 292, 324-327.
- Goldstein, S.L., O'Nions, R.K., and Hamilton, P.J. (1984). A Sm-Nd isotopic study of atmospheric dusts and particulates from major river systems. Earth and Planetary Science Letters 70, 221-236.
- Goodwin, A. (1991). Precambrian Geology: The Dynamic Evolution of the Continental Crust. Academic Press, London (666 pg.).
- Gordon, A.L. (1986). Interocean exchange of thermocline water. Journal of Geophysical Research: Oceans 91, 5037-5046.
- Goswami, V., Singh, S.K., and Bhushan, R. (2014). Impact of water mass mixing and dust deposition on Nd concentration and ε_{Nd} of the Arabian Sea water column. Geochimica et Cosmochimica Acta 145, 30-49.
- Goswami, V., Singh, S.K., Bhushan, R., and Rai, V.K. (2012). Temporal variations in 87 Sr/ 86 Sr and ε_{Nd} in sediments of the southeastern Arabian Sea: Impact of monsoon and surface water circulation. Geochemistry, Geophysics, Geosystems 13, n/a-n/a.
- Gupta, L.P., Subramanian, V., and Ittekkot, V. (1997). Biogeochemistry of particulate organic matter transported by the Godavari River, India. Biogeochemistry 38, 103-128.

- Haley, B.A., Frank, M., Hathorne, E., and Pisias, N. (2014). Biogeochemical implications from dissolved rare earth element and Nd isotope distributions in the Gulf of Alaska. Geochimica et Cosmochimica Acta 126, 455-474.
- Hathorne, E.C., Stichel, T., Brück, B., and Frank, M. (2015). Rare earth element distribution in the Atlantic sector of the Southern Ocean: The balance between particle scavenging and vertical supply. Marine Chemistry 177, Part 1, 157-171.
- Hatje, V., Bruland, K.W., and Flegal, A.R. (2014). Determination of rare earth elements after pre-concentration using NOBIAS-chelate PA-1®resin: Method development and application in the San Francisco Bay plume. Marine Chemistry 160, 34-41.
- Hatje, V., Payne, T.E., Hill, D.M., McOrist, G., Birch, G.F., and Szymczak, R. (2003). Kinetics of trace element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading. Environment International 29, 619-629.
- Henderson, G.M. (2016). Ocean trace element cycles. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 374.
- Hess, J., Bender, M., and Schilling, J. (1986). Seawater ⁸⁷Sr/⁸⁶Sr evolution from Cretaceous to present-Applications to paleoceanography. Science 231, 979-984.
- Hodell, D.A., Kamenov, G.D., Hathorne, E.C., Zachos, J.C., Röhl, U., and Westerhold, T. (2007). Variations in the strontium isotope composition of seawater during the Paleocene and early Eocene from ODP Leg 208 (Walvis Ridge). Geochemistry, Geophysics, Geosystems 8, n/a-n/a.

- Hodell, D.A., Mead, G.A., and Mueller, P.A. (1990). Variation in the strontium isotopic composition of seawater (8 Ma to present).: Implications for chemical weathering rates and dissolved fluxes to the oceans. Chemical Geology: Isotope Geoscience section 80, 291-307.
- Hodges, K.V., Wobus, C., Ruhl, K., Schildgen, T., and Whipple, K. (2004). Quaternary deformation, river steepening, and heavy precipitation at the front of the Higher Himalayan ranges. Earth and Planetary Science Letters 220, 379-389.
- Homoky, W.B., Weber, T., Berelson, W.M., Conway, T.M., Henderson, G.M., van Hulten, M., Jeandel, C., Severmann, S., and Tagliabue, A. (2016).Quantifying trace element and isotope fluxes at the ocean-sediment boundary: a review. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 374.
- Hoyle, J., Elderfield, H., Gledhill, A., and Greaves, M. (1984). The behaviour of the rare earth elements during mixing of river and sea waters. Geochimica et Cosmochimica Acta 48, 143-149.
- Huang, K.F., You, C.F., Chung, C.H., and Lin, I.T. (2011). Nonhomogeneous seawater Sr isotopic composition in the coastal oceans: A novel tool for tracing water masses and submarine groundwater discharge. Geochemistry, Geophysics, Geosystems 12.
- Huh, Y. (2003). Chemical weathering and climate a global experiment: a review. Geosciences Journal 7, 277-288.
- Iyengar, S.V.P., Chandy, K.C., and Narayanswamy, R. (1981). Geochronology and Rb-Sr systematics of the igneous rocks of Simlipal Complex, Orissa, India. Indian Journal of Earth Sciences 8, 61-65.
- Jacobsen, S.B., and Wasserburg, G.J. (1980). Sm-Nd isotopic evolution of chondrites. Earth and Planetary Science Letters 50, 139-155.

- Jain, S.K., Agarwal, P.K., and Singh, V.P. (2007). Hydrology and Water Resources of India. Springer.
- Jayananda, M., Chardon, D., Peucat, J.J., and Capdevila, R. (2006). 2.61 Ga potassic granites and crustal reworking in the western Dharwar craton, southern India: Tectonic, geochronologic and geochemical constraints. Precambrian Research 150, 1-26.
- Jayananda, M., Kano, T., Peucat, J.J., and Channabasappa, S. (2008). 3.35 Ga komatiite volcanism in the western Dharwar craton, southern India: Constraints from Nd isotopes and whole-rock geochemistry. Precambrian Research 162, 160-179.
- Jayananda, M., Moyen, J.F., Martin, H., Peucat, J.J., Auvray, B., and Mahabaleswar, B. (2000). Late Archaean (2550-2520 Ma). juvenile magmatism in the Eastern Dharwar craton, southern India: constraints from geochronology, Nd-Sr isotopes and whole rock geochemistry. Precambrian Research 99, 225-254.
- Jayananda, M., Peucat, J.J., Chardon, D., Rao, B.K., Fanning, C.M., and Corfu, F. (2013a). Neoarchean greenstone volcanism and continental growth, Dharwar craton, southern India: Constraints from SIMS U-Pb zircon geochronology and Nd isotopes. Precambrian Research 227, 55-76.
- Jayananda, M., Tsutsumi, Y., Miyazaki, T., Gireesh, R.V., Kapfo, K.-u., Tushipokla, Hidaka, H., and Kano, T. (2013b). Geochronological constraints on Meso- and Neoarchean regional metamorphism and magmatism in the Dharwar craton, southern India. Journal of Asian Earth Sciences 78, 18-38.
- Jeandel, C. (1993). Concentration and isotopic composition of Nd in the South Atlantic Ocean. Earth and Planetary Science Letters 117, 581-591.

- Jeandel, C. (2016). Overview of the mechanisms that could explain the 'Boundary Exchange' at the land-ocean contact. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 374.
- Jeandel, C., Bishop, J.K., and Zindler, A. (1995). Exchange of neodymium and its isotopes between seawater and small and large particles in the Sargasso Sea. Geochimica et Cosmochimica Acta 59, 535-547.
- Jeandel, C., Thouron, D., and Fieux, M. (1998). Concentrations and isotopic compositions of neodymium in the eastern Indian Ocean and Indonesian straits. Geochimica et Cosmochimica Acta 62, 2597-2607.
- Jha, P.K., Tiwari, J., Singh, U.K., Kumar, M., and Subramanian, V. (2009). Chemical weathering and associated CO₂ consumption in the Godavari river basin, India. Chemical Geology 264, 364-374.
- Johannesson, K.H., Chevis, D.A., Burdige, D.J., Cable, J.E., Martin, J.B., and Roy, M. (2011). Submarine groundwater discharge is an important net source of light and middle REEs to coastal waters of the Indian River Lagoon, Florida, USA. Geochimica et Cosmochimica Acta 75, 825-843.
- Jones, C.E., and Jenkyns, H.C. (2001). Seawater Strontium Isotopes, Oceanic Anoxic Events, and Seafloor Hydrothermal Activity in the Jurassic and Cretaceous. American Journal of Science 301, 112-149.
- Keller, G., Adatte, T., Bhowmick, P., Upadhyay, H., Dave, A., Reddy, A., and Jaiprakash, B. (2012). Nature and timing of extinctions in Cretaceous-Tertiary planktic foraminifera preserved in Deccan intertrappean sediments of the Krishna-Godavari Basin, India. Earth and Planetary Science Letters 341, 211-221.
- Khansa Zaidi, Sarwar Rais, Abdullah Khan, and Alam, M.M. (2014). Provenance, Tectonics and Paleoclimate of Permo-Carboniferous Talchir Formation in Son-Mahanadi Basin, Central India with Special Reference to Chirimiri:

Using Petrographical Interpretation. International Journal of Geosciences 5, 122-130.

- Kim, G., Ryu, J.-W., Yang, H.-S., and Yun, S.-T. (2005). Submarine groundwater discharge (SGD). into the Yellow Sea revealed by 228Ra and 226Ra isotopes: Implications for global silicate fluxes. Earth and Planetary Science Letters 237, 156-166.
- Kim, I., and Kim, G. (2014). Submarine groundwater discharge as a main source of rare earth elements in coastal waters. Marine Chemistry 160, 11-17.
- Kim, I., and Kim, G. (2015). Role of colloids in the discharge of trace elements and rare earth elements from coastal groundwater to the ocean. Marine Chemistry 176, 126-132.
- Kim, G., and Hwang, D.-W. (2002). Tidal pumping of groundwater into the coastal ocean revealed from submarine 222Rn and CH4 monitoring. Geophysical Research Letters 29, 23-21-23-24.
- Knight, K.B., Renne, P.R., Halkett, A., and White, N. (2003). ⁴⁰Ar/³⁹Ar dating of the Rajahmundry Traps, Eastern India and their relationship to the Deccan Traps. Earth and Planetary Science Letters 208, 85-99.
- Konhauser, K.O., Powell, M.A., Fyfe, W.S., Longstaffe, F.J., and Tripathy, S. (1997). Trace element geochemistry of river sediment, Orissa State, India. Journal of Hydrology 193, 258-269.
- Kotwicki, L., Grzelak, K., Czub, M., Dellwig, O., Gentz, T., Szymczycha, B., and Böttcher, M. (2014). Submarine groundwater discharge to the Baltic coastal zone: Impacts on the meiofaunal community. Journal of Marine Systems 129, 118-126.
- Krest, J., Moore, W., Gardner, L., and Morris, J. (2000). Marsh nutrient export supplied by groundwater discharge: Evidence from radium measurements. Global Biogeochemical Cycles 14, 167-176.

- Krishnan, M.S. (1982). Geology of India and Burma. 6th ed. CBS Publications and Distributions, Madras.
- Krishnaswami, S., and Singh, S.K. (1998). Silicate and carbonate weathering in the drainage basins of the Ganga-Ghaghara-Indus head waters: Contributions to major ion and Sr isotope geochemistry. Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences 107, 283-291.
- Krishnaswami, S., and Singh, S.K. (2005). Chemical weathering in the river basins of the Himalaya, India. Current Science 89, 841-849.
- Krishnaswami, S., Singh, S., and Dalai, T. (1999). Silicate weathering in the Himalaya: role in contributing to major ions and radiogenic Sr to the Bay of Bengal. Ocean Science, Trends and Future Directions, 23-51.
- Krishnaswami, S., Trivedi, J., Sarin, M., Ramesh, R., and Sharma, K. (1992).
 Strontium isotopes and rubidium in the Ganga-Brahmaputra river system:
 Weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic ⁸⁷Sr/⁸⁶Sr. Earth and Planetary Science Letters 109, 243-253.
- Kump, L.R., Brantley, S.L., and Arthur, M.A. (2000). Chemical weathering, atmospheric CO₂, and climate. Annual Review of Earth and Planetary Sciences 28, 611-667.
- Lee, D.-C., Halliday, A.N., Hein, J.R., Burton, K.W., Christensen, J.N., and Günther, D. (1999). Hafnium Isotope Stratigraphy of Ferromanganese Crusts. Science 285, 1052-1054.
- Licht, A., France-Lanord, C., Reisberg, L., Fontaine, C., Soe, A.N., and Jaeger, J.-J. (2013). A palaeo Tibet-Myanmar connection? Reconstructing the Late Eocene drainage system of central Myanmar using a multi-proxy approach. Journal of the Geological Society 170, 929-939.

- Liew, T.C., and McCulloch, M.T. (1985). Genesis of granitoid batholiths of Peninsular Malaysia and implications for models of crustal evolution: Evidence from a Nd-Sr isotopic and U-Pb zircon study. Geochimica et Cosmochimica Acta 49, 587-600.
- Lightfoot, P. and Hawkesworth, C. (1988). Origin of Deccan Trap lavas: evidence from combined trace element and Sr-Nd and Pb-isotope studies. Earth and Planetary Science Letters 91, 89-104.
- Lin, I.-T., Wang, C.-H., You, C.-F., Lin, S., Huang, K.-F., and Chen, Y.-G. (2010). Deep submarine groundwater discharge indicated by tracers of oxygen, strontium isotopes and barium content in the Pingtung coastal zone, southern Taiwan. Marine Chemistry 122, 51-58.
- Lupker, M., Aciego, S.M., Bourdon, B., Schwander, J., and Stocker, T.F. (2010). Isotopic tracing (Sr, Nd, U and Hf). of continental and marine aerosols in an 18th century section of the Dye-3 ice core (Greenland). Earth and Planetary Science Letters 295, 277-286.
- Mackey, D.J., O'Sullivan, J.E.O., and Watson, R.J. (2002). Iron in the western Pacific: a riverine or hydrothermal source for iron in the Equatorial Undercurrent? Deep Sea Research Part I: Oceanographic Research Papers 49, 877-893.
- Madhupratap, M., Kumar, S.P., Bhattathiri, P., Kumar, M.D., Raghukumar, S., Nair, K., and Ramaiah, N. (1996). Mechanism of the biological response to winter cooling in the northeastern Arabian Sea. Nature 384, 549-552.
- Maher, B., Prospero, J., Mackie, D., Gaiero, D., Hesse, P., and Balkanski, Y. (2010). Global connections between aeolian dust, climate and ocean biogeochemistry at the present day and at the last glacial maximum. Earth-Science Reviews 99, 61-97.
- Mahoney, J.J., Sheth, H.C., Chandrasekharam, D., and Peng, Z.X. (2000). Geochemistry of Flood Basalts of the Toranmal Section, Northern Deccan 287 | P a g e

Traps, India: Implications for Regional Deccan Stratigraphy. Journal of Petrology 41, 1099-1120.

- Manikyamba, C., Ganguly, S., Santosh, M., Saha, A., and Lakshminarayana, G. (2015). Geochemistry and petrogenesis of Rajahmundry trap basalts of Krishna-Godavari Basin, India. Geoscience Frontiers 6, 437-451.
- Mantyla, A.W. and Reid, J.L. (1995). On the origins of deep and bottom waters of the Indian Ocean. Journal of Geophysical Research: Oceans 100, 2417-2439.
- Martin, J.M., Høgdahl, O., and Philippot, J. (1976). Rare earth element supply to the ocean. Journal of Geophysical Research 81, 3119-3124.
- Maury, R.C., Pubellier, M., Rangin, C., Wulput, L., Cotten, J., Socquet, A., Bellon, H., Guillaud, J.-P., and Htun, H.M. (2004). Quaternary calcalkaline and alkaline volcanism in an hyper-oblique convergence setting, central Myanmar and western Yunnan. Bulletin de la Societe Geologique de France 175, 461-472.
- Measures, C., and Vink, S. (1999). Seasonal variations in the distribution of Fe and Al in the surface waters of the Arabian Sea. Deep Sea Research Part II: Topical Studies in Oceanography 46, 1597-1622.
- Measures, C.I., and Vink, S. (2000). On the use of dissolved aluminum in surface waters to estimate dust deposition to the ocean. Global Biogeochemical Cycles 14, 317-327.
- Meybeck, M. (1987). Global chemical weathering of surficial rocks estimated from river dissolved loads. American Journal of Science 287, 401-428.
- Middag, R., de Baar, H.J.W., Laan, P., Cai, P.H., and van Ooijen, J.C. (2011).Dissolved manganese in the Atlantic sector of the Southern Ocean. Deep Sea Research Part II: Topical Studies in Oceanography 58, 2661-2677.

- Millot, R., Gaillardet, J.é., Dupré, B., and Allègre, C.J. (2003). Northern latitude chemical weathering rates: clues from the Mackenzie River Basin, Canada. Geochimica et Cosmochimica Acta 67, 1305-1329.
- Mishra, S., Deomurari, M.P., Wiedenbeck, M., Goswami, J.N., Ray, S., and Saha, A.K. (1999). ²⁰⁷Pb/²⁰⁶Pb zircon ages and the evolution of the Singhbhum Craton, eastern India: an ion microprobe study1. Precambrian Research 93, 139-151.
- Mondal, S.K., Frei, R., and Ripley, E.M. (2007). Os isotope systematics of mesoarchean chromitite-PGE deposits in the Singhbhum Craton (India).: Implications for the evolution of lithospheric mantle. Chemical Geology 244, 391-408.
- Moon, S., Huh, Y., Qin, J., and van Pho, N. (2007). Chemical weathering in the Hong (Red). River basin: Rates of silicate weathering and their controlling factors. Geochimica et Cosmochimica Acta 71, 1411-1430.
- Moore, W.S. (2010). The effect of submarine groundwater discharge on the ocean. Annual review of marine science 2, 59-88.
- Morel, F.M.M., Hudson, R.J.M., and Price, N.M. (1991). Limitation of productivity by trace metals in the sea. Limnology and Oceanography 36, 1742-1755.
- Mukhopadhyay, G., Mukhopadhyay, S.K., Roychowdhury, M., and Parui, P.K. (2010). Stratigraphic correlation between different Gondwana Basins of India. Journal of the Geological Society of India 76, 251-266.
- Mukhopadhyay, J., Beukes, N.J., Armstrong, R.A., Zimmermann, U., Ghosh, G., and Medda, R.A. (2008). Dating the Oldest Greenstone in India: A 3.51-Ga Precise U-Pb SHRIMP Zircon Age for Dacitic Lava of the Southern Iron Ore Group, Singhbhum Craton. The Journal of Geology 116, 449-461.

- Nair, R., Ittekkot, V., Manganini, S., Ramaswamy, V., Haake, B., Degens, E., Desai, B.t., and Honjo, S. (1989). Increased particle flux to the deep ocean related to monsoons.
- Najman, Y., Bickle, M., BouDagher-Fadel, M., Carter, A., Garzanti, E., Paul, M., Wijbrans, J., Willett, E., Oliver, G., Parrish, R., Akhter, S.H., Allen, R., Ando, S., Chisty, E., Reisberg, L., and Vezzoli, G. (2008). The Paleogene record of Himalayan erosion: Bengal Basin, Bangladesh. Earth and Planetary Science Letters 273, 1-14.
- Najman, Y., Johnson, K., White, N., and Oliver, G. (2004). Evolution of the Himalayan foreland basin, NW India. Basin Research 16, 1-24.
- Nakapadungrat, S., Beckinsale, R., and Suensilpong, S. (1984). Geochronology and geology of Thai granites, Proceedings of the Conference on Applications of Geology and the National Development. Chulalongkorn University, Bangkok, pp. 75-93.
- Naqvi, S.M. and Rogers, J.J.W. (1987). Precambrian geology of India. Oxford University Press.
- Négrel, P., Allègre, C.J., Dupré, B., and Lewin, E. (1993). Erosion sources determined by inversion of major and trace element ratios and strontium isotopic ratios in river water: The Congo Basin case. Earth and Planetary Science Letters 120, 59-76.
- Nelson, D.R., Bhattacharya, H.N., Thern, E.R., and Altermann, W. (2014). Geochemical and ion-microprobe U-Pb zircon constraints on the Archaean evolution of Singhbhum Craton, eastern India. Precambrian Research 255, Part 1, 412-432.

- Nesbitt, H.W., and Young, G.M. (1982). Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature 299, 715-717.
- Nowell, G.M., Kempton, P.D., Noble, S.R., Fitton, J.G., Saunders, A.D., Mahoney, J.J., and Taylor, R.N. (1998). High precision Hf isotope measurements of MORB and OIB by thermal ionisation mass spectrometry: insights into the depleted mantle. Chemical Geology 149, 211-233.
- Nozaki, Y., and Alibo, D.S. (2003). Importance of vertical geochemical processes in controlling the oceanic profiles of dissolved rare earth elements in the northeastern Indian Ocean. Earth and Planetary Science Letters 205, 155-172.
- O'Connor, A.E., Luek, J.L., McIntosh, H., and Beck, A.J. (2015). Geochemistry of redox-sensitive trace elements in a shallow subterranean estuary. Marine Chemistry 172, 70-81.
- Oliver, L., Harris, N., Bickle, M., Chapman, H., Dise, N., and Horstwood, M. (2003). Silicate weathering rates decoupled from the ⁸⁷Sr/⁸⁶Sr ratio of the dissolved load during Himalayan erosion. Chemical Geology 201, 119-139.
- Palmer, M., and Edmond, J. (1989). The strontium isotope budget of the modern ocean. Earth and Planetary Science Letters 92, 11-26.
- Palmer, M., and Edmond, J. (1992). Controls over the strontium isotope composition of river water. Geochimica et Cosmochimica Acta 56, 2099-2111.
- Palmer, M., and Elderfield, H. (1985). Sr isotope composition of sea water over the past 75 Myr.

- Panda, D.K., Kumar, A., and Mohanty, S. (2011). Recent trends in sediment load of the tropical (Peninsular) river basins of India. Global and Planetary Change 75, 108-118.
- Parwin R. (2014). Assessment of Water Resources & Management Strategies of Brahmani River Basin. M.Tech. NIT, Rourkela, Odisha, 1-121.
- Patchett, P.J., Tatsumoto, M., 1980. Hafnium isotope variations in oceanic basalts. Geophysical Research Letters 7, 1077-1080.
- Paytan, A., Shellenbarger, G.G., Street, J.H., Gonneea, M.E., Davis, K., Young, M.B., and Moore, W.S. (2006). Submarine groundwater discharge: An important source of new inorganic nitrogen to coral reef ecosystems. Limnology and Oceanography 51, 343-348.
- Peng, Z.X., Mahoney, J., Hooper, P., Harris, C., and Beane, J. (1994). A role for lower continental crust in flood basalt genesis? Isotopic and incompatible element study of the lower six formations of the western Deccan Traps. Geochimica et Cosmochimica Acta 58, 267-288.
- Peng, Z.X., Mahoney, J.J., Vanderkluysen, L., and Hooper, P.R. (2014). Sr, Nd and Pb isotopic and chemical compositions of central Deccan Traps lavas and relation to southwestern Deccan stratigraphy. Journal of Asian Earth Sciences 84, 83-94.
- Piepgras, D.J., Wasserburg, G.J., and Dasch, E.J. (1979). The isotopic composition of Nd in different ocean masses. Earth and Planetary Science Letters 45, 223-236.
- Pierson-Wickmann, A.-C., Reisberg, L., France-Lanord, C., and Kudrass, H.R. (2001). Os-Sr-Nd results from sediments in the Bay of Bengal: Implications for sediment transport and the marine Os record. Paleoceanography 16, 435-444.

- Pillai, A.G., Naik, M.S., Momin, G.A., Rao, P.S.P., Safai, P.D., Ali, K., Rodhe, H., and Granat, L. (2001). Studies of Wet Deposition and Dustfall at Pune, India. Water, Air, and Soil Pollution 130, 475-480.
- Piotrowski, A.M., Lee, D.-C., Christensen, J.N., Burton, K.W., Halliday, A.N., Hein, J.R., and Günther, D. (2000). Changes in erosion and ocean circulation recorded in the Hf isotopic compositions of North Atlantic and Indian Ocean ferromanganese crusts. Earth and Planetary Science Letters 181, 315-325.
- Piotrowski, A.M., Banakar, V.K., Scrivner, A.E., Elderfield, H., Galy, A., and Dennis, A. (2009). Indian Ocean circulation and productivity during the last glacial cycle. Earth and Planetary Science Letters 285, 179-189.
- Potemra, J.T., Luther, M.E., and O'Brien, J.J. (1991). The seasonal circulation of the upper ocean in the Bay of Bengal. Journal of Geophysical Research: Oceans 96, 12667-12683.
- Probst, J.L., Mortatti, J., and Tardy, Y. (1994). Carbon river fluxes and weathering CO2 consumption in the Congo and Amazon river basins. Applied Geochemistry 9, 1-13.
- Quade, J., English, N., and DeCelles, P.G. (2003). Silicate versus carbonate weathering in the Himalaya: a comparison of the Arun and Seti River watersheds. Chemical Geology 202, 275-296.
- Rahaman, W., and Singh, S.K. (2010). Rhenium in rivers and estuaries of India: Sources, transport and behaviour. Marine Chemistry 118, 1-10.
- Rahaman, W., and Singh, S.K. (2012). Sr and ⁸⁷Sr/⁸⁶Sr in estuaries of western India: Impact of submarine groundwater discharge. Geochimica et Cosmochimica Acta 85, 275-288.

- Rahaman, W., Singh, S.K., and Raghav, S. (2010). Dissolved Mo and U in rivers and estuaries of India: Implication to geochemistry of redox sensitive elements and their marine budgets. Chemical Geology 278, 160-172.
- Rahaman, W., Singh, S.K., Sinha, R., and Tandon, S.K. (2011). Sr, C and O isotopes in carbonate nodules from the Ganga Plain: Evidence for recent abrupt rise in dissolved ⁸⁷Sr/⁸⁶Sr ratios of the Ganga. Chemical Geology 285, 184-193.
- Rahmstorf, S. (2002). Ocean circulation and climate during the past 120,000 years. Nature 419, 207-214.
- Rai, S.K., and Singh, S.K. (2007). Temporal variation in Sr and ⁸⁷Sr/⁸⁶Sr of the Brahmaputra: Implications for annual fluxes and tracking flash floods through chemical and isotope composition. Geochemistry, Geophysics, Geosystems 8.
- Rai, S.K., Singh, S.K., and Krishnaswami, S. (2010). Chemical weathering in the plain and peninsular sub-basins of the Ganga: Impact on major ion chemistry and elemental fluxes. Geochimica et Cosmochimica Acta 74, 2340-2355.
- Ramakrishnan, M., and Vaidyanadhan, R. (2008). Geology of India. Geological society of India, Bangalore.
- Raman, C., Rao, G.K., Reddy, K., Ramesh, M. (1995). Clay mineral distributions in the continental shelf sediments between the Ganges mouths and Madras, east coast of India. Continental Shelf Research 15, 1773-1793.
- Ramaswamy, V., Gaye, B., Shirodkar, P.V., Rao, P.S., Chivas, A.R., Wheeler, D., and Thwin, S. (2008). Distribution and sources of organic carbon, nitrogen and their isotopic signatures in sediments from the Ayeyarwady (Irrawaddy). continental shelf, northern Andaman Sea. Marine Chemistry 111, 137-150.

- Ramaswamy, V., and Nair, R. (1994). Fluxes of material in the Arabian Sea and Bay of Bengal—sediment trap studies. Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences 103, 189-210.
- Ramaswamy, V., Rao, P.S., Rao, K.H., Thwin, S., Rao, N.S., and Raiker, V. (2004). Tidal influence on suspended sediment distribution and dispersal in the northern Andaman Sea and Gulf of Martaban. Marine Geology 208, 33-42.
- Rao, G.D., and Sarma, V.V. (2013). Contribution of N₂O emissions to the atmosphere from Indian monsoonal estuaries. 2013, 65.
- Rao, K.L. (1975). India's Water Wealth. Orient Longman Ltd., New Delhi.
- Rao, P., Ramaswamy, V., and Thwin, S. (2005). Sediment texture, distribution and transport on the Ayeyarwady continental shelf, Andaman Sea. Marine Geology 216, 239-247.
- Raymo, M.E. (1994). The Himalayas, organic carbon burial, and climate in the Miocene. Paleoceanography 9, 399-404.
- Raymo, M., and Ruddiman, W.F. (1992). Tectonic forcing of late Cenozoic climate. Nature 359, 117-122.
- Reddy, S., Clark, C., and Mazumder, R.(2008). Was there any pre-Nuna India-Antarctic connection? Evidence from SHRIMP U–Pb zircon dating. In: 33rd IGC Conference Abstracts 33, #1344159.
- Rempfer, J., Stocker, T.F., Joos, F., Dutay, J.-C., and Siddall, M. (2011).
 Modelling Nd-isotopes with a coarse resolution ocean circulation model:
 Sensitivities to model parameters and source/sink distributions.
 Geochimica et Cosmochimica Acta 75, 5927-5950.
- Rengarajan, R., and Sarma, V. (2015). Submarine groundwater discharge and nutrient addition to the coastal zone of the Godavari estuary. Marine Chemistry 172, 57-69.

- Rengarajan, R., Singh, S.K., Sarin, M.M., and Krishnaswami, S. (2009). Strontium isotopes and major ion chemistry in the Chambal River system, India: Implications to silicate erosion rates of the Ganga. Chemical Geology 260, 87-101.
- Resing, J.A., Sedwick, P.N., German, C.R., Jenkins, W.J., Moffett, J.W., Sohst,B.M., and Tagliabue, A. (2015). Basin-scale transport of hydrothermal dissolved metals across the South Pacific Ocean. Nature 523, 200-203.
- Rhein, M. (1995). Deep water formation in the western Mediterranean. Journal of Geophysical Research: Oceans 100, 6943-6959.
- Richter, F.M., Rowley, D.B., and DePaolo, D.J. (1992). Sr isotope evolution of seawater: the role of tectonics. Earth and Planetary Science Letters 109, 11-23.
- Rickli, J., Frank, M., Baker, A., Aciego, S., De Souza, G., Georg, R., and Halliday, A. (2010). Hafnium and neodymium isotopes in surface waters of the eastern Atlantic Ocean: Implications for sources and inputs of trace metals to the ocean. Geochimica et Cosmochimica Acta 74, 540-557.
- Rickli, J., Frank, M., and Halliday, A.N. (2009). The hafnium-neodymium isotopic composition of Atlantic seawater. Earth and Planetary Science Letters 280, 118-127.
- Rickli, J., Gutjahr, M., Vance, D., Fischer-Gödde, M., Hillenbrand, C.-D., and Kuhn, G. (2014). Neodymium and hafnium boundary contributions to seawater along the West Antarctic continental margin. Earth and Planetary Science Letters 394, 99-110.
- Robinson, R.A.J., Bird, M., Oo, N.W., Hoey, T., Aye, M.M., Higgitt, D., Lu, X., Swe, A., Tun, T., and Win, S.L. (2007). The Irrawaddy River sediment flux to the Indian Ocean: the original nineteenth-century data revisited. The Journal of Geology 115, 629-640.
- Rochford, D. (1964). Salinity maxima in the upper 1000 metres of the North Indian Ocean. Marine and Freshwater Research 15, 1-24.

- Roddick, J.C., Sullivan, R.W., and Dudas, F.O. (1992). Precise calibration of tracer compositions for Sm-Nd isotopic studies. Geological Survey of Canada 91, 191-200.
- Rodolfo, K.S. (1969). Sediments of the Andaman basin, northeastern Indian Ocean. Marine Geology 7, 371-402.
- Rousseau, T.C.C., Sonke, J.E., Chmeleff, J., Candaudap, F., Lacan, F., Boaventura, G., Seyler, P., and Jeandel, C. (2013). Rare earth element analysis in natural waters by multiple isotope dilution - sector field ICP-MS. Journal of Analytical Atomic Spectrometry 28, 573-584.
- Rousseau, T.C., Sonke, J.E., Chmeleff, J., van Beek, P., Souhaut, M., Boaventura, G., Seyler, P., and Jeandel, C. (2015). Rapid neodymium release to marine waters from lithogenic sediments in the Amazon estuary. Nature communications 6.
- Roy-Barman, M., Wasserburg, G.J., Papanastassiou, D.A., and Chaussidon, M. (1998). Osmium isotopic compositions and Re–Os concentrations in sulfide globules from basaltic glasses. Earth and Planetary Science Letters 154, 331-347.
- Ruddiman, W.F. (1997). Tropical Atlantic terrigenous fluxes since 25,000 yrsB.P. Marine Geology 136, 189-207.
- Saager, P.M., De Baar, H.J., and Burkill, P.H. (1989). Manganese and iron in Indian Ocean waters. Geochimica et Cosmochimica Acta 53, 2259-2267.
- Salve, P.R., Maurya, A., Sinha, R., Gawane, A.G., and Wate, S.R. (2006). Characterization and Source Identification of Major Inorganic Ions in Precipitation of Nagpur, India. Bulletin of Environmental Contamination and Toxicology 77, 305-311.
- Salve, P.R., Maurya, A., Wate, S.R., and Devotta, S. (2008). Chemical Composition of Major Ions in Rainwater. Bulletin of Environmental Contamination and Toxicology 80, 242-246.

- Sanyal, S., and Sengupta, P. (2012). Metamorphic evolution of the Chotanagpur Granite Gneiss Complex of the East Indian Shield: current status. Geological Society, London, Special Publications 365, 117-145.
- Sarin, M., and Krishnaswami, S. (1984). Major ion chemistry of the Ganga-Brahmaputra river systems, India.
- Sarin, M., Krishnaswami, S., Dilli, K., Somayajulu, B., and Moore, W. (1989). Major ion chemistry of the Ganga-Brahmaputra river system: Weathering processes and fluxes to the Bay of Bengal. Geochimica et cosmochimica acta 53, 997-1009.
- Sarin, M., Krishnaswami, S., Trivedi, J., and Sharma, K. (1992). Major ion chemistry of the Ganga source waters: weathering in the high altitude Himalaya. Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences 101, 89-98.
- Sarin, M., Sudheer, A., and Balakrishna, K. (2002). Significance of riverine carbon transport: A case study of a large tropical river, Godavari (India). SCIENCE IN CHINA SERIES C LIFE SCIENCES-ENGLISH EDITION-45, 97-108.
- Sarkar, G., Corfu, F., Paul, D.K., McNaughton, N.J., Gupta, S.N., and Bishui, P.K. (1993). Early Archean crust in Bastar Craton, Central India—a geochemical and isotopic study. Precambrian Research 62, 127-137.
- Sarkar, S., and Saha, A. (1977). The present status of the Precambrian stratigraphy, tectonics and geochronology of Singhbhum-Keonjhar-Mayurbhanj region, eastern India. Indian J. Earth Sci 4, 37-65.
- Sarkar, S., and Saha, A. (1983). Structure and tectonics of the Singhbhum-Orissa iron ore craton, eastern India. Recent researches in Geology 10, 1-25.
- Sarkar, S., Saha, A., Boelrijk, N., and Hebeda, E. (1979). New data on the geochronology of the Older Metamorphic Group and the Singhbhum

Granite of Singhbhum-Keonjhar-Mayurbhanj region, eastern India. Indian J. Earth Sci 6, 32-51.

- Sarkar, A., Sarkar, G., Paul, D., and Mitra, N. (1990). Precambrian geochronology of the central Indian shield—a review. Geol. Surv. India, Spec. Publ 28, 353-382.
- Sarma, V.V.S.S., Prasad, V.R., Kumar, B.S.K., Rajeev, K., Devi, B.M.M., Reddy, N.P.C., Sarma, V.V., and Kumar, M.D. (2010). Intra-annual variability in nutrients in the Godavari estuary, India. Continental Shelf Research 30, 2005-2014.
- Sarma, V., Viswanadham, R., Rao, G., Prasad, V., Kumar, B., Naidu, S., Kumar, N., Rao, D., Sridevi, T., and Krishna, M. (2012). Carbon dioxide emissions from Indian monsoonal estuaries. Geophysical Research Letters 39.
- Schoene, B., Samperton, K.M., Eddy, M.P., Keller, G., Adatte, T., Bowring, S.A., Khadri, S.F., and Gertsch, B. (2015). U-Pb geochronology of the Deccan Traps and relation to the end-Cretaceous mass extinction. Science 347, 182-184.
- Schott, F.A., and McCreary Jr, J.P. (2001). The monsoon circulation of the Indian Ocean. Progress in Oceanography 51, 1-123.
- Schulz, H., von Rad, U., and Erlenkeuser, H. (1998). Correlation between Arabian Sea and Greenland climate oscillations of the past 110,000 years. Nature 393, 54-57.
- Shenoi, S., Shetye, S., Gouveia, A., and Michael, G. (1993). Salinity extrema in the Arabian Sea. Mitteilungen des Geologisch-Paläontologischen Instituts der Universität Hamburg SCOPE/UNEP Sonderband 76, 37-49.

- Shenoi, S.S.C., Saji, P.K., and Almeida, A.M. (1999). Near-surface circulation and kinetic energy in the tropical Indian Ocean derived from Lagrangian drifters. Journal of Marine Research 57, 885-907.
- Shetye, S., Gouveia, A., and Shenoi, S (1994). Circulation and water masses of the Arabian Sea. Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences 103, 107-123.
- Shimmield, G.B., and Price, N.B. (1986). The behaviour of molybdenum and manganese during early sediment diagenesis — offshore Baja California, Mexico. Marine Chemistry 19, 261-280.
- Sholkovitz, E., and Szymczak, R. (2000). The estuarine chemistry of rare earth elements: comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems. Earth and Planetary Science Letters 179, 299-309.
- Sholkovitz, E.R. (1976). Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochimica et Cosmochimica Acta 40, 831-845.
- Sholkovitz, E.R. (1993). The geochemistry of rare earth elements in the Amazon River estuary. Geochimica et Cosmochimica Acta 57, 2181-2190.
- Singh, S.K. (2006). Spatial variability in erosion in the Brahmaputra basin: causes and impacts. Current Science 90, 1272-1275.
- Singh, S.K., and France-Lanord, C. (2002). Tracing the distribution of erosion in the Brahmaputra watershed from isotopic compositions of stream sediments. Earth and Planetary Science Letters 202, 645-662.
- Singh, S.K., Kumar, A., and France-Lanord, C. (2006). Sr and ⁸⁷Sr/⁸⁶Sr in waters and sediments of the Brahmaputra river system: Silicate weathering, CO₂ consumption and Sr flux. Chemical Geology 234, 308-320.
- Singh, S.K., Rai, S.K., and Krishnaswami, S. (2008). Sr and Nd isotopes in river sediments from the Ganga Basin: Sediment provenance and spatial

variability in physical erosion. Journal of Geophysical Research: Earth Surface (2003-2012). 113.

- Singh, S.K., Sarin, M., and France-Lanord, C. (2005). Chemical erosion in the eastern Himalaya: major ion composition of the Brahmaputra and δ^{13} C of dissolved inorganic carbon. Geochimica et Cosmochimica Acta 69, 3573-3588.
- Singh, S.K., Trivedi, J.R., Pande, K., Ramesh, R., and Krishnaswami, S. (1998). Chemical and Strontium, Oxygen, and Carbon Isotopic Compositions of Carbonates from the Lesser Himalaya: Implications to the Strontium Isotope Composition of the Source Waters of the Ganga, Ghaghara, and the Indus Rivers. Geochimica et Cosmochimica Acta 62, 743-755.
- Singh, S.P., Singh, S.K., Goswami, V., Bhushan, R., and Rai, V.K. (2012). Spatial distribution of dissolved neodymium and ε_{Nd} in the Bay of Bengal: role of particulate matter and mixing of water masses. Geochimica et Cosmochimica Acta 94, 38-56.
- Singh, Y., and Krishna, V. (2009). Rb-Sr geochronology and petrogenesis of granitoids from the Chhotanagpur granite gneiss complex of Raikera-Kunkuri region, Central India. Journal of the Geological Society of India 74, 200-208.
- Sinha, P., Jena, G., Jain, I., Rao, A., and Husain, M.L. (2010). Numerical modelling of tidal circulation and sediment transport in the Gulf of Khambhat and Narmada Estuary, west coast of India. Pertanika Journal of Science & Technology 18, 293-302.
- Sirocko, F. (1995). Abrupt change in monsoonal climate: Evidence from the geochemical composition of Arabian sea sediments, Habilitation thesis, University of Kiel.
- Sirocko, F., and Sarnthein, M. (1989). Wind-borne deposits in the northwestern Indian Ocean: Record of Holocene sediments versus modern satellite data,
Paleoclimatology and paleometeorology: modern and past patterns of global atmospheric transport. Springer, pp. 401-433.

- Stephenson, D., and Marshall, T.R. (1984). The petrology and mineralogy of Mt. Popa Volcano and the nature of the late-Cenozoic Burma Volcanic Arc. Journal of the Geological Society 141, 747-762.
- Stichel, T., Frank, M., Rickli, J., and Haley, B.A. (2012). The hafnium and neodymium isotope composition of seawater in the Atlantic sector of the Southern Ocean. Earth and Planetary Science Letters 317-318, 282-294.
- Subramanian, V. (1979). Chemical and suspended-sediment characteristics of rivers of India. Journal of Hydrology 44, 37-55.
- Sullivan, R.W., and Roddick, J.C. (1992). Preparation and concentration calibration of a mixed 149Sm-148Nd tracer solution used for Sm-Nd geochronology and tracer studies in the Geochronology Laboratory, Geological Survey of Canada: In Radiogenic Age and Isotopic Studies. Geological Survey of Canada 91, 200-205.
- Sundaray, S.K. (2010). Application of multivariate statistical techniques in hydrogeochemical studies—a case study: Brahmani-Koel River (India). Environmental Monitoring and Assessment 164, 297-310.
- Sundaray, S.K., Nayak, B.B., and Bhatta, D. (2009). Environmental studies on river water quality with reference to suitability for agricultural purposes: Mahanadi river estuarine system, India - a case study. Environmental Monitoring and Assessment 155, 227-243.
- Szulc, A.G., Najman, Y., Sinclair, H.D., Pringle, M., Bickle, M., Chapman, H., Garzanti, E., Andò, S., Huyghe, P., Mugnier, J.L., Ojha, T., and DeCelles, P. (2006). Tectonic evolution of the Himalaya constrained by detrital 40Ar-39Ar, Sm-Nd and petrographic data from the Siwalik foreland basin succession, SW Nepal. Basin Research 18, 375-391.

- Tachikawa, K., Athias, V., and Jeandel, C. (2003). Neodymium budget in the modern ocean and paleo-oceanographic implications. Journal of Geophysical Research: Oceans 108.
- Tachikawa, K., Jeandel, C., and Roy-Barman, M. (1999). A new approach to the Nd residence time in the ocean: the role of atmospheric inputs. Earth and Planetary Science Letters 170, 433-446.
- Tagliabue, A., Bopp, L., Dutay, J.-C., Bowie, A.R., Chever, F., Jean-Baptiste, P., Bucciarelli, E., Lannuzel, D., Remenyi, T., Sarthou, G., Aumont, O., Gehlen, M., and Jeandel, C. (2010). Hydrothermal contribution to the oceanic dissolved iron inventory. Nature Geosci 3, 252-256.
- Tarantola, A. (2005). The least square criterion. Inverse Problem Theory and Methods for Model Parameter Estimation, 68-72.
- Taylor, S.R., and McLennan, S.M. (1985). The Continental Crust: Its Composition and Evolution. Carlton: Blackwell Scientific Publication.
- Taylor, S.R., and McLennan, S.M. (1995). The geochemical evolution of the continental crust. Reviews of Geophysics 33, 241-265.
- Thiede, R.C., Bookhagen, B., Arrowsmith, J.R., Sobel, E.R., and Strecker, M.R. (2004). Climatic control on rapid exhumation along the Southern Himalayan Front. Earth and Planetary Science Letters 222, 791-806.
- Tipper, E.T., Bickle, M.J., Galy, A., West, A.J., Pomiès, C., and Chapman, H.J. (2006). The short term climatic sensitivity of carbonate and silicate weathering fluxes: Insight from seasonal variations in river chemistry. Geochimica et Cosmochimica Acta 70, 2737-2754.
- Tripathy, G.R., Goswami, V., Singh, S.K., and Chakrapani, G. (2010). Temporal variations in Sr and ⁸⁷Sr/⁸⁶Sr of the Ganga headwaters: estimates of dissolved Sr flux to the mainstream. Hydrological Processes 24, 1159-1171.

- Tripathy, G.R., and Singh, S.K. (2010). Chemical erosion rates of river basins of the Ganga system in the Himalaya: Reanalysis based on inversion of dissolved major ions, Sr, and ⁸⁷Sr/⁸⁶Sr. Geochemistry, Geophysics, Geosystems 11.
- Tripathy, G.R., Singh, S.K., Bhushan, R., and Ramaswamy, V. (2011). Sr-Nd isotope composition of the Bay of Bengal sediments: Impact of climate on erosion in the Himalaya. Geochemical Journal 45, 175-186.
- Tripathy, G.R., Singh, S.K., and Krishnaswami, S. (2012). Sr and Nd isotopes as tracers of chemical and physical erosion, Handbook of Environmental Isotope Geochemistry. Springer, pp. 521-552.
- Trivedi, J., Pande, K., Krishnaswami, S., and Sarin, M. (1995). Sr isotopes in rivers of India and Pakistan: A reconnaissance study. CURRENT SCIENCE-BANGALORE- 69, 171-171.
- Tütken, T., Eisenhauer, A., Wiegand, B., and Hansen, B.T. (2002). Glacialinterglacial cycles in Sr and Nd isotopic composition of Arctic marine sediments triggered by the Svalbard/Barents Sea ice sheet. Marine Geology 182, 351-372.
- Unger, D., Ittekkot, V., Schäfer, P., Tiemann, J., and Reschke, S. (2003). Seasonality and interannual variability of particle fluxes to the deep Bay of Bengal: influence of riverine input and oceanographic processes. Deep Sea Research Part II: Topical Studies in Oceanography 50, 897-923.
- van de Flierdt, T., Frank, M., Halliday, A.N., Hein, J.R., Hattendorf, B., Günther, D., and Kubik, P.W. (2004a). Tracing the history of submarine hydrothermal inputs and the significance of hydrothermal hafnium for the seawater budget—a combined Pb-Hf-Nd isotope approach. Earth and Planetary Science Letters 222, 259-273.

- van de Flierdt, T., Frank, M., Lee, D.-C., and Halliday, A.N. (2002). Glacial weathering and the hafnium isotope composition of seawater. Earth and Planetary Science Letters 198, 167-175.
- van de Flierdt, T., Frank, M., Lee, D.-C., Halliday, A.N., Reynolds, B.C., and Hein, J.R. (2004b). New constraints on the sources and behavior of neodymium and hafnium in seawater from Pacific Ocean ferromanganese crusts. Geochimica et Cosmochimica Acta 68, 3827-3843.
- van de Flierdt, T., Goldstein, S.L., Hemming, S.R., Roy, M., Frank, M., and Halliday, A.N. (2007). Global neodymium-hafnium isotope systematics revisited. Earth and Planetary Science Letters 259, 432-441.
- van de Flierdt, T., Griffiths, A.M., Lambelet, M., Little, S.H., Stichel, T., and Wilson, D.J. (2016). Neodymium in the oceans: a global database, a regional comparison and implications for palaeoceanographic research. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences 374.
- van de Flierdt, T., Hemming, S.R., Goldstein, S.L., Abouchami, W. (2006). Radiogenic isotope fingerprint of Wilkes Land–Adélie Coast Bottom Water in the circum-Antarctic Ocean. Geophysical Research Letters 33, L12606.
- Veizer, J. (1989). Strontium isotopes in seawater through time. Annual Review of Earth and Planetary Sciences 17, 141.
- Vervoort, J.D., Patchett, P.J., Blichert-Toft, J., and Albarède, F. (1999). Relationships between Lu–Hf and Sm–Nd isotopic systems in the global sedimentary system. Earth and Planetary Science Letters 168, 79-99.
- Viers, J., Roddaz, M., Filizola, N., Guyot, J.-L., Sondag, F., Brunet, P., Zouiten, C., Boucayrand, C., Martin, F., and Boaventura, G.R. (2008). Seasonal and provenance controls on Nd-Sr isotopic compositions of Amazon rivers

suspended sediments and implications for Nd and Sr fluxes exported to the Atlantic Ocean. Earth and Planetary Science Letters 274, 511-523.

- Vohra, C.P., Dasgupta, S., Paul, D.K., Bishui, P.K., Gupta, S.N., and Guha, S. (1991). Rb-Sr Chronology and Petrochemistry of Granitoids from the South-Eastern Part of the Singhbhum Craton, Orissa.
- Vuba, S., Ahmad, S.M., and Anipindi, N.R. (2015). Geochemical and mineralogical studies in recent clastic sediments from upper Godavari river in peninsular India. Journal of the Geological Society of India 86, 107-114.
- Walter, H.J., Hegner, E., Diekmann, B., Kuhn, G., and Rutgers van der loeff, M.M. (2000). Provenance and transport of terrigenous sediment in the south Atlantic Ocean and their relations to glacial and interglacial cycles: Nd and Sr isotopic evidence. Geochimica et Cosmochimica Acta 64, 3813-3827.
- Wani, H., and Mondal, M.E.A. (2011). Evaluation of provenance, tectonic setting, and paleoredox conditions of the Mesoproterozoic-Neoproterozoic basins of the Bastar craton, Central Indian Shield: Using petrography of sandstones and geochemistry of shales. Lithosphere 3, 143-154.
- Wang, Z., Liu, C., Han, G., and Xu, Z. (2001). Strontium isotopic geochemistry of the Changjiang estuarine waters: Implications for water-sediment interaction. Science in China Series E: Technological Sciences 44, 129-133.
- Ward, L.G., Michael Kemp, W., and Boynton, W.R. (1984). The influence of waves and seagrass communities on suspended particulates in an estuarine embayment. Marine Geology 59, 85-103.

- White, A.F., and Blum, A.E. (1995). Effects of climate on chemical_weathering in watersheds. Geochimica et Cosmochimica Acta 59, 1729-1747.
- White, A.F., Blum, A.E., Bullen, T.D., Vivit, D.V., Schulz, M., and Fitzpatrick, J. (1999a). The effect of temperature on experimental and natural chemical weathering rates of granitoid rocks. Geochimica et Cosmochimica Acta 63, 3277-3291.
- White, A.F., Bullen, T.D., Vivit, D.V., Schulz, M.S., and Clow, D.W. (1999b). The role of disseminated calcite in the chemical weathering of granitoid rocks. Geochimica et Cosmochimica Acta 63, 1939-1953.
- Win, S.H. (2011). Sediment Dynamics in Irrawaddy River, Myanmar.
- Windom, H., Smith, R., Niencheski, F., and Alexander, C. (2000). Uranium in rivers and estuaries of globally diverse, smaller watersheds. Marine Chemistry 68, 307-321.
- Windom, H.L., Moore, W.S., Niencheski, L.F.H., and Jahnke, R.A. (2006). Submarine groundwater discharge: A large, previously unrecognized source of dissolved iron to the South Atlantic Ocean. Marine Chemistry 102, 252-266.
- Winter, B.L., Johnson, C.M., and Clark, D.L. (1997). Strontium, neodymium, and lead isotope variations of authigenic and silicate sediment components from the Late Cenozoic Arctic Ocean: Implications for sediment provenance and the source of trace metals in seawater. Geochimica et Cosmochimica Acta 61, 4181-4200.
- Wobus, C., Heimsath, A., Whipple, K., and Hodges, K. (2005). Active out-ofsequence thrust faulting in the central Nepalese Himalaya. Nature 434, 1008-1011.
- Woods, J.D. (1985). The world ocean circulation experiment.

- Wu, L., Huh, Y., Qin, J., Du, G., and van Der Lee, S. (2005). Chemical weathering in the Upper Huang He (Yellow River). draining the eastern Qinghai-Tibet Plateau. Geochimica et Cosmochimica Acta 69, 5279-5294.
- Wyrtki, K. (1973). "Physicaloceanography of the Indian Ocean" in The biology of the Indian Ocean. Springer, New York, NY.
- Xu, Y., and Marcantonio, F. (2004). Speciation of strontium in particulates and sediments from the Mississippi River mixing zone1. Geochimica et Cosmochimica Acta 68, 2649-2657.
- Xu, Y., and Marcantonio, F. (2007). Strontium isotope variations in the lower Mississippi River and its estuarine mixing zone. Marine Chemistry 105, 118-128.
- Yang, H.-S., Hwang, D.-W., and Kim, G. (2002). Factors controlling excess radium in the Nakdong River estuary, Korea: submarine groundwater discharge versus desorption from riverine particles. Marine Chemistry 78, 1-8.
- Yang, Y., Zhang, H., Xie, L., and Wu, F. (2008). Accurate measurement of neodymium isotopic composition using Neptune MC-ICP-MS. Frontiers of Chemistry in China 3, 94-98.
- Yang, Y.H., Hong-Fu, Z., Lie-Wen, X., and Fu-Yuan, W. (2007). Accurate measurement of neodymium isotopic composition using Neptune multiple collector inductively coupled plasma mass spectrometry. Chinese Journal of Analytical Chemistry 35, 71.
- Yeats, P.A. and Bewers, J.M. (1976). Trace metals in the waters of the Saguenay fjord. Canadian Journal of Earth Sciences 13, 1319-1327.
- Yeghicheyan, D., Carignan, J., Valladon, M., Le Coz, M.B., Cornec, F.L., Castrec-Rouelle, M., Robert, M., Aquilina, L., Aubry, E., Churlaud, C., 308 | P a g e

Dia, A., Deberdt, S., Dupré, B., Freydier, R., Gruau, G., Hénin, O., de Kersabiec, A.-M., Macé, J., Marin, L., Morin, N., Petitjean, P., and Serrat, E. (2001). A Compilation of Silicon and Thirty One Trace Elements Measured in the Natural River Water Reference Material SLRS-4 (NRC-CNRC). Geostandards Newsletter 25, 465-474.

- You, Y. (2000). Implications of the deep circulation and ventilation of the Indian Ocean on the renewal mechanism of North Atlantic Deep Water. Journal of Geophysical Research: Oceans 105, 23895-23926.
- Zektser, I.S., and Loaiciga, H.A. (1993). Groundwater fluxes in the global hydrologic cycle: past, present and future. Journal of Hydrology 144, 405-427.
- Zimmermann, B., Porcelli, D., Frank, M., Andersson, P.S., Baskaran, M., Lee, D.-C., and Halliday, A.N. (2009a). Hafnium isotopes in Arctic Ocean water. Geochimica et Cosmochimica Acta 73, 3218-3233.
- Zimmermann, B., Porcelli, D., Frank, M., Rickli, J., Lee, D.-C., and Halliday, A.N. (2009b). The hafnium isotope composition of Pacific Ocean water. Geochimica et Cosmochimica Acta 73, 91-101.

LIST OF PUBLICATION

Research publications

 K. Damodararao, Sunil K. Singh, Vinai K. Rai, V. Ramaswamy and P.S. Rao, (2016). Lithology, monsoon and sea-surface current control on provenance, dispersal and deposition of sediments over the Andaman continental shelf, Front. Mar. Sci. 3:118. doi: 10.3389/fmars.2016.00118.

Articles (Under Preparation):

- K. Damodararao, Gyana R. Tripathy, Sunil K. Singh and Vinai K. Rai, Chemical weathering in the Mahanadi and Brahmani River basins: Impact on major ions chemistry and radiogenic Sr and their fluxes to the Bay of Bengal.
- K. Damodararao and Sunil K. Singh, Fractionation of rare earth elements and Nd isotope composition during weathering in the Godavari River System.
- 3. K. Damodararao, Sunil K. Singh and Vinai K. Rai, Chemical weathering in the Godavari River system: Impact on carbon cycle and trace elements budgets of the Bay of Bengal.
- 4. K. Damodararao, Sunil K. Singh and Vinai K. Rai, Dissolved Strontium concentration and its isotope composition in the mixing zone of the Eastern India Estuaries: Implications to the submarine groundwater discharge and contribution to the global marine Sr isotope budget.

- K. Damodararao, and Sunil K. Singh, Massive release of trace elements and isotopes in the Ganga (Hooghly) and other East Indian estuaries: Implication to their modern Oceanic budgets.
- 6. K. Damodararao, Sunil K. Singh and Vinai K. Rai, Tracking the erosion pattern in the Godavari River system based on Sr-Nd isotope composition of particulates: Controlling factors and impacts.
- 7. K. Damodararao, Sunil K. Singh, Vineet Goswami and Ravi Bhushan, Dissolved Neodymium and its isotope composition in the Arabian Sea: Water Mass mixing vs. particle – water interaction.
- 8. K.Damodararao, Sunil K. Singh, Vineet Goswami, Ravi Bhushan and R. Rengarajan, The Hafnium concentration and its isotope composition in water columns of the Indian Ocean: Implications to its sources and Water Mass mixing patterns.

Abstracts (Conferences/Symposium):

- K. Damodararao and Sunil K. Singh, Dissolved Sr and its isotopes in estuaries of eastern coast of India: Impact of submarine groundwater discharge. 28th ISMAS symposium cum workshop on mass spectrometry, Parwanoo (India), March 9-13, 2014.
- K. Damodararao, Sunil K. Singh, Ravi Bhushan and Vinai K. Rai. ε_{Nd} in the Arabian Sea: Water Mass mixing vs. particle – water interaction. 25th Goldschmidt conference at Prague, Czech Republic, August 16-21, 2015.
- 3. K. Damodararao, Sunil K. Singh and Vinai K. Rai. Dissolved Sr and ⁸⁷Sr/⁸⁶Sr in the East Indian Estuaries: Inferences to submarine groundwater discharge. International Symposium on the Indian Ocean at Goa, India, November 30 – December 4, 2015.

4. **K. Damodararao**, Sunil K. Singh and Vinai K. Rai. REEs and ε_{Nd} in the Ganga (Hooghly) and other East Indian Estuaries: Massive desorption of particulate REEs to the Ocean. 26th Goldschmidt conference at Yokohama, Japan, June 26 - July 2, 2016.





Lithology, Monsoon and Sea-Surface Current Control on Provenance, Dispersal and Deposition of Sediments over the Andaman Continental Shelf

Karri Damodararao¹, Sunil K. Singh^{1*}, Vinai K. Rai¹, V. Ramaswamy² and P. S. Rao²

¹ Physical Research Laboratory, Ahmedabad, India, ² National Institute of Oceanography, Goa, India

OPEN ACCESS

Edited by:

Selvaraj Kandasamy, Xiamen University, China

Reviewed by:

Liviu Giosan, Woods Hole Oceanographic Institution, USA Ludvig Löwemark, National Taiwan University, Taiwan Armstrong-Altrin John S., Universidad Nacional Autónoma de México, Mexico

> *Correspondence: Sunil K. Singh sunil@prl.res.in

Specialty section:

This article was submitted to Marine Biogeochemistry, a section of the journal Frontiers in Marine Science

Received: 22 April 2016 **Accepted:** 22 June 2016 **Published:** 14 July 2016

Citation:

Damodararao K, Singh SK, Rai VK, Ramaswamy V and Rao PS (2016) Lithology, Monsoon and Sea-Surface Current Control on Provenance, Dispersal and Deposition of Sediments over the Andaman Continental Shelf. Front. Mar. Sci. 3:118. doi: 10.3389/fmars.2016.00118

Sediments deposited on the Northern and Eastern Andaman Shelf along with a few sediments from the Irrawaddy and the Salween Rivers are studied for their elemental, Sr and Nd concentrations and their isotope composition to identify their sources, constrain their transport pathways and to assess the factors influencing the erosion in the catchment and their dispersal and deposition over the Andaman Shelf region. Major elemental compositions of the shelf sediments suggest mafic lithology such as ophiolites, ultrabasic rocks, and andesites in the Irrawaddy drainage and over Indo-Burman-Arakan (IBA) ranges as their dominant source. ⁸⁷Sr/⁸⁶Sr ratios in sediments of the Northern and Eastern Andaman Shelf range between 0.712245 and 0.742183 whereas, ε_{Nd} varie from -6.29 to -17.25. Sediments around Mergui have the highest ⁸⁷Sr/⁸⁶Sr and the lowest ε_{Nd} values. Sr and Nd isotope compositions of these sediments along with that in the potential sources suggest four major sources of these sediments to the Andaman Shelf, (i) the Irrawaddy River, (ii) the Salween River, (iii) Rivers draining the IBA ranges and (vi) Rivers draining the Western/Central granitic ranges of the Southern Myanmar and Western Thailand such as the Tavoy and the Tanintharyi Rivers. Erosion in the catchment is controlled by the precipitation and topography. Intensely focused precipitation over the higher relief of the western slopes of the IBA and Western/Central granitic ranges causes higher erosion over this mountainous region, supplying huge sediments through the Kaladan, Irrawaddy, Salween, and the Tanintharyi Rivers to the Western Myanmar Shelf, Northern, and Eastern Andaman Shelves respectively. The majority of the sediments produced in the drainage are delivered to the shelf during the south-west monsoon which is dispersed eastward by sea-surface circulation from the mouth of the Irrawaddy Rivers toward the Gulf of Martaban and further southward. The Andaman Shelf receives very little sediment, if any, from the Ganga-Brahmaputra Delta. Higher erosion over the Western/Central granitic belt of the Southern Myanmar and Western Thailand and its importance in delivering sediments through the rivers draining its western slope such as the Tanintharyi and the Tavoy Rivers to the Eastern Andaman Shelf around the Mergui Archipelago are highlighted for the first time in this study.

Keywords: Andaman Shelf, Myanmar, sediments, biogeochemistry, Sr-Nd isotopes, erosion, climate, precipitation

1

INTRODUCTION

Rivers are the primary transporters of physically and/or chemically weathered continental materials to the ocean. They play a prominent role in the evolution of coastal and deep sea sediments. Terrigenous sediments eroded from the Himalayas, Myanmar, and Indo-Burman subcontinents are deposited to the Andaman Sea by rivers such as the Irrawaddy (Ayeyarwaddy), the Salween (Thanlwin), the Sittang, the Kaladan and the Tanintharyi etc. The Irrawaddy is the third largest river in the world in terms of suspended sediment discharge and together with the Salween contributes \sim 550 million tons (MT) of sediment annually (Robinson et al., 2007). Intense monsoon causes higher runoff in the Irrawaddy Basin, which in turn enhances erosion in the catchment area. The sediments brought by the Irrawaddy and the Salween Rivers are deposited in the Northern and Eastern Andaman Shelf with a width of more than 170 km. A significant amount of terrestrial organic matter brought by these rivers is deposited along with them influencing the long-term carbon cycle (France-Lanord and Derry, 1997; Bird et al., 2008; Ramaswamy et al., 2008). The sources of these sediments deposited on Northern and Eastern Andaman Shelf and the factors controlling the erosion of this large volume of sediments are poorly constrained due to complicated logistic and political reasons associated with their sampling. The seasonally reversing surface circulation controlled by the monsoon (Rodolfo, 1969; Ramaswamy et al., 2004; Rao et al., 2005) influences the dispersion and deposition of these sediments significantly. Influence of the Irrawaddy and the Salween Rivers on the sedimentary budget of the Eastern Bay of Bengal (BoB) is still a matter of debate, though they deliver huge amount of sediments into the Andaman Sea (Rao et al., 2005; Robinson et al., 2007). The sediments deposited in the Andaman Sea brought down by these river systems, preserve imprints of the erosion and weathering history of Himalayan and Burman Ranges (Colin et al., 1999). Detrital sediments are primarily the weathered products of continental rocks with a wide range of Sr and Nd isotope ratios. The distinct isotopic compositions of these sediments can be used to track their provenance (Goldstein et al., 1984; Colin et al., 1999; Galy and France-Lanord, 2001; Singh and France-Lanord, 2002; Singh et al., 2008; Tripathy et al., 2011; Goswami et al., 2012). In the present study, the Sr and Nd isotopic composition and major elemental concentrations of silicate fractions of surface sediments of the Northern and Eastern Andaman Shelf are measured to track their provenances. Further, an effort has been made to evaluate the role of climate and tectonics in controlling the erosion in its catchment and to assess the impact of surface ocean circulation in controlling the dispersal and deposition of these sediments.

STUDY AREA

Andaman Shelf Basin

Andaman is a unique basin, which is separated from Bay of Bengal by the Andaman-Nicobar Ridge. The Irrawaddy and the Salween Rivers are the major sedimentary sources to the Andaman Basin. Together they supply about 550 MT (Irrawaddy: \sim 364 MT and Salween: \sim 180 MT; Robinson et al., 2007) sediment load to the Andaman Sea annually. The shelf width is about 170 km off the Irrawaddy River mouth and increases to more than 250 km in the center of the Gulf of Martaban (**Figure 1**). A N–S trending 120 km wide bathymetric depression is present toward the southern end of the continental shelf and the Martaban submarine canyon lies within this depression (Rao et al., 2005).

Tidal currents and the seasonally reversing monsoon currents strongly influence the sediment spreading on the Irrawaddy continental shelf (Figure 1; Wyrtki, 1973; Ramaswamy et al., 2004; Rao et al., 2005). The south-west (SW) monsoon is active during May-October and 80-90% of the annual Myanmar rainfall, runoff and sediment discharge occur during this period, whereas the north-east (NE) monsoon is active between December and February (Rodolfo, 1969; Rao et al., 2005). During the SW monsoon, Myanmar receives very high precipitation and at places it is highly intense and focused. The western slopes of the Indo-Burmese and Western/Central granitic ranges receive rainfall as high as 5 m/y (Figure 2). Higher precipitation in the catchment produces higher erosion and transport a large quantity of sediments to the Andaman Sea. The sediment fluxes of the Irrawaddy River to the Andaman Sea during 1966-1996 indicate significant yearly and monthly variations (Win, 2011) and most of these sediments are delivered to the sea during the SW monsoon period (Win, 2011). In response to the monsoons, the oceanic flow of surface waters in the Andaman Sea changes direction annually two times with a cyclonic flow in the spring and summer and anti-cyclonic flow for the rest of the year (Potemra et al., 1991). Surface current in the Andaman Sea flows east- and southward (blue arrows, Figure 1) during SW monsoon which reverses during NW monsoon (red arrows, Figure 1). Current and winds during the SW monsoon drive the surface ocean eastward transferring the turbid Irrawaddy discharge from the river's mouths.

The Irrawaddy continental shelf and the Gulf of Martaban are covered by a modern inner-shelf mud belt while relict sands and carbonates cover the outer shelf (Rodolfo, 1969; Rao et al., 2005). High suspended sediment in the Gulf of Martaban and Irrawaddy continental shelf is a continual feature due to macrotidal setting (Ramaswamy et al., 2004). A significant fraction of the suspended sediment delivered by the Irrawaddy River is transported eastward and deposited in the Gulf of Martaban along with those brought by the Salween River. A smaller fraction is transported into the Eastern BoB between October and December. Transport of the suspended sediments as bottom flows directly into the deep Andaman Sea via the Martaban Canyon is also seen (Ramaswamy et al., 2004). Sediments deposited on the South-Eastern Andaman Shelf could be derived from the Southern Myanmar and the Western Thailand (Rodolfo, 1969).

Geology of the Catchment Area

The Northern and Eastern Andaman shelves receive sediments mainly through the Irrawaddy and Salween Rivers. The Irrawaddy is the major river originating in the Northern



Myanmar with a catchment area of 4.1×10^5 km² and debouching into the Andaman Sea (Robinson et al., 2007). The Chindwin is its major tributary which joins it in downstream Mandalay. The Salween River is much longer, ~2800 km, with



http://trmm.gsfc.nasa.gov/).

a catchment area $\sim 2.7 \times 10^5$ km² (Robinson et al., 2007). It originates in the Tibetan Plateau, flows through Yunnan Province of China, the Kayan and the Mon States of Myanmar and debouches into the Gulf of Martaban in the Andaman Sea. Most of the sediments delivered to the Andaman Sea are brought by the Irrawaddy and the Salween Rivers. Smaller rivers such as the Kaladan, Naf, Lemro, Mayu, etc. flowing through the western slope of the Indo–Burman ranges along the Arakan (Rakhine) coast supply sediments to the western shelf of Myanmar, whereas smaller rivers of Southern Myanmar, such as the Heinze, Ye, Tavoy, Tanintharyi and the Lenya flowing through the mountains of Southern Myanmar and Western Thailand contribute sediments to the Eastern Andaman Shelf.

The rivers bringing sediments to the Andaman Shelf drain various lithologies in their catchments. The major lithologies these rivers drain are presented in **Figure 3**. The Irrawaddy River flows, in its upper reaches, through the Gangdese batholith, metamorphic rocks and ophiolites of



possible eastern continuation of the Indus Tsangpo Suture Zone, the volcanics from a Cretaceous arc and sediments produced during the collision (Stephenson and Marshall, 1984; Maury et al., 2004; Najman et al., 2004; Szulc et al., 2006; Allen et al., 2008), associated post-collision intrusive igneous rocks (Darbyshire and Swainbank, 1988) and basic/ultrabasic rocks of the eastern syntaxis of the Himalaya. In the middle reaches, the Irrawaddy drains the Mogok Metamorphic Belt containing schists, gneisses, marble, migmatites, and calc-alkaline plutonics (Figure 3; Chapman et al., 2015). The catchment of the Irrawaddy River east of Mogok Metamorphic Belt comprises the older Palaeozoic sediments of the Asian Plate origin form the highlands of the Shan Plateau incorporating turbidites and carbonates. A significant part of the Irrawaddy basin lies in the Central Troughs (Eastern and Western Troughs, Figure 3) which comprises late Cretaceous and younger sediments with granite-granodiorite intrusions and alkaline andesite-dacite volcanoes. The Miocene granitic rocks extend from the south of Mandalay toward Western Thailand.

Many of the rivers along the Arakan coast and the western tributaries of the Irrawaddy such as the Chindwin River drain the Indo–Burman hills comprising the Neogene and Paleogene sedimentary rocks, ophiolites, serpentinites and metamorphic rocks of Triassic to Cretaceous age (**Figure 3**). The Indo–Burman hills contain Cretaceous-Cenozoic forearc flysch (Allen et al., 2008).

The Salween River drains the magmatic belt with Trans-Himalayan batholith of the Northern Lhasa block and Precambrian to Tertiary sedimentary, igneous and metamorphic rocks of the Shan Plateau/Sibumashu block (**Figure 3**; Nakapadungrat et al., 1984).

Rivers such as the Tanintharyi and the Tavoy that drain the Southern Myanmar and Western Thailand flow through the Western and Central granitic belts (Figure 3; Nakapadungrat et al., 1984; Liew and McCulloch, 1985).

Materials and Methods

A total of 110 surface sediment samples were collected from the Northern Andaman Shelf region during the low river discharge period of April-May, 2002 onboard the 175th expedition of ORV Sagar Kanya (Figure 1; Ramaswamy et al., 2008). Geochemical elements, Sr, Nd concentrations and Sr-Nd isotopic compositions of about fifty sediment samples were investigated in this study. The sediments were dried in an oven at $\sim 50^{\circ}$ C and powdered to $<100 \ \mu m$ using an agate mortar and pestle. The geochemical elements abundances and Sr-Nd isotopic analyses of the samples were carried out in their silicate fractions. Toward this, the bulk samples (number of shelf sediments, n = 46) were decarbonated using 0.6N HCl and ashed at 600°C to oxidize the organic matter. These decarbonated and organic matter free samples were dissolved by repeated treatment of HF-HNO3-HCl acids (Potts, 1992). Abundances of major elements (e.g., Ca, Mg, Fe, Mn, Al, and Ti) in these solutions were measured using an ICP-AES (Horiba, Jobin-Yvon, Ultima), whereas Na and K were measured using Flame-AAS (Perkin-Elmer). SiO2 could not be determined as it got evaporated as SiF₄ during the sample dissolution with HF followed by subsequent evaporation (Potts, 1992). A few samples were analyzed in replicate to determine the precision of measurements; these replicate measurements show that the analytical reproducibility of the geochemical analysis is better than 5 wt%. The accuracy of these measurements was ascertained by analyzing NIST standard SDO-1 and SCo-1 along with samples. Sr-Nd isotopic analyses in the silicate fractions were carried out following established analytical methodology at Physical Research Laboratory, Ahmedabad, India (Singh et al., 2008; Goswami et al., 2012). The silicate fraction of the samples, together with known amount of ⁸⁴Sr spike was digested completely using HF-HNO3-HCl acids. Pure fractions of Sr and Nd were separated from the solution using conventional column chromatography (Singh et al., 2008). Measurements of Sr and Nd isotopes were carried out using Thermo Neptune MC-ICP-MS in static multi collection mode (Goswami et al., 2012). The isotope data were corrected for instrumental mass fractionation by normalizing the Sr and Nd isotopic data with ⁸⁶Sr/⁸⁸Sr (=0.1194) and ¹⁴⁶Nd/¹⁴⁴Nd (=0.7219) respectively. The Sr concentrations in samples were determined using isotope dilution whereas Nd contents were determined using standard calibration methods by QICP-MS (Thermo Xseries-2). During the course of this study, the measurement of isotopic composition of Sr and Nd of known international standards were also carried out. The average ⁸⁷Sr/⁸⁶Sr ratio of standard SRM 987 during these measurements, 0.710332 \pm 0.000010; (1 σ , n = 8) and ¹⁴³Nd/¹⁴⁴Nd for Merck Nd 0.511702 \pm 0.000010; $(1\sigma, n = 8)$ were found consistent with their published values. The total procedural blank for Sr and Nd for these analyses were found few orders of magnitude lower than Sr and Nd processed in samples and hence data were not corrected for blank. Along with shelf sediments, three riverine sediments, one from the Irrawaddy mouth and two from the Salween were also analyzed for their major, Sr, Nd elemental abundances and Sr and Nd isotope compositions following the above protocols.

RESULTS

The Northern and Eastern Andaman Shelf sediment samples analyzed in this study are dominated by silt and clay fractions (Rodolfo, 1969; Rao et al., 2005; Ramaswamy et al., 2008) with coarser sand dispersed at places. The concentrations of major elements such as Na, K, Ca, Mg, Al, Fe, Mn, and Ti measured in silicate fraction of the shelf and river sediments are reported in Table 1. The relative abundances of these elements in the shelf sediments were observed in an increasing order, Mn < Ti < Ca < Na < Mg < K < Fe < Al. This trend originates in large extent from the earth crust through weathering. The concentrations of major elements display a large variation (Table 1). Al is the most abundant in most of the samples followed by Fe. Al and Fe vary from 0.5 to 13.1 wt% and 0.5 to 6.1 wt% respectively, which are within the typical range for rock forming minerals (Alagarsamy et al., 2010). A few sediment samples collected near the Mergui shelf along Southern Myanmar (Figure 1) contain lower content of Al and other elements probably due to the dominance of quartz in them. Ca varies from 0.07 to 0.94 wt% in these de-carbonated samples. Al and Fe contents in Irrawaddy River sediment are high, 12 and 6 wt% respectively whereas they are \sim 6 and 3 wt% respectively in Salween River sediments. The concentrations and isotopic compositions of Sr and Nd of shelf and river sediments are presented in Table 1. The ranges of Sr and Nd concentrations are 10–162 μ g/g and 2.4–38.6 μ g/g respectively and are generally lower or comparable to the values reported for Irrawaddy, Salween, and Ganga-Brahmaputra (G-B) River sediments (Colin et al., 1999; Singh et al., 2008). The ⁸⁷Sr/⁸⁶Sr and ε_{Nd} values of shelf sediments vary from 0.712245 to 0.742183 and -6.29 to -17.25 respectively. Higher ϵ_{Nd} values were found for samples from the Western Myanmar coast, which usually have low ⁸⁷Sr/⁸⁶Sr. Sediments collected from Mergui shelf region have most radiogenic Sr and least radiogenic Nd, similar to those reported in the Ganga-Brahmaputra Rivers (Galy and France-Lanord, 2001). Sediments from off Salween River contain higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $\epsilon_{Nd}.$ Sr and Nd isotope compositions of sediments collected from the Gulf of Martban are intermediate to the two extremes defined by sediments of the Arakan (Rakhine) coast and that of the Salween mouth and the Mergui shelf. The Irrawaddy and the Salween River sediments have contrasting Sr and Nd isotope composition; Irrawaddy has lesser radiogenic Sr and more radiogenic Nd when compared to that of the Salween. Sr and Nd isotope compositions of the Salween sediments are comparable to that of the lower Meghna (Combined Ganga and Brahmaputra, G-B) in Bangladesh (Galy and France-Lanord, 2001).

DISCUSSION

Major Element Compositions and Implications for Provenance

In this study chemical composition has been determined in the silicate fraction of the sediments. Al and Fe display large variability in these sediments. Part of these variabilities result from their source effect whereas weathering and size sorting TABLE 1 | Sample locations, major element compositions, concentrations, and isotope compositions of Sr and Nd and Chemical Index of Alteration (CIA) in surface sediment samples from the Irrawaddy continental shelf, Northern Andaman Sea and the Irrawaddy and the Salween Rivers.

Station no.	Latitude	Longitude	Na ₂ O	к ₂ 0	CaO	MgO	Al_2O_3	Fe ₂ O ₃	MnO	TiO ₂	[Sr]	⁸⁷ Sr/ ⁸⁶ Sr	[Nd]	¹⁴³ Nd/ ¹⁴⁴ Nd	ε _{Nd} (0)	CIA
						v	vt %				μ g/g		μ g/g			
SK-175/3	17°29.47′	94°27.50′	1.02	2.30	0.17	2.51	24.77	7.64	0.031	0.94	54	0.716734	19.3	0.512315	-6.3	88
SK-175/5	16°59.35′	94°20.78′	1.12	1.32	0.45	1.44	13.25	5.30	0.034	0.74	162	0.713101	19.6	0.512268	-7.2	82
SK-175/10	16°29.73′	94°10.00'	1.47	1.03	0.76	1.02	8.28	3.91	0.030	0.76	108	0.713014	18.5	0.512162	-9.3	72
SK-175/14	16°00.03′	93°44.37′	0.62	1.15	0.37	1.23	9.79	5.51	0.035	0.70	65	0.716388	18.5	0.512104	-10.4	82
SK-175/20	15°29.95′	94°00.03′	0.46	1.16	0.37	0.57	3.12	2.62	0.020	0.34	57	0.713403	7.3	0.512044	-11.6	61
SK-175/22	15°30.83′	94°30.33′	1.29	1.00	0.98	1.28	5.88	3.96	0.044	0.44	113	0.713586	10.9	0.512076	-11.0	64
SK-175/24	15°16.12′	94°44.65′	1.41	1.26	1.03	1.41	7.41	3.49	0.030	0.43	128	0.712245	4.5	0.512075	-11.0	67
SK-175/26	15°00.39′	94°15.21′	1.29	1.39	0.81	1.28	10.82	3.31	0.029	0.64	100	0.715966	17.9	0.512162	-9.3	76
SK-175/27	14°59.67′	94°00.13′	0.66	1.38	0.53	0.53	5.08	2.00	0.019	0.30	76	0.715593	2.4	0.512069	-11.1	66
SK-175/32	14°29.88′	94°45.00′	1.37	1.44	0.84	1.60	11.46	4.17	0.038	0.65	95	0.715572	18.7	0.512077	-10.9	76
SK-175/34	14°44.98′	94°59.88′	1.25	1.56	0.80	1.49	10.25	4.01	0.037	0.54	148	0.714846	14.1	0.512101	-10.5	74
SK-175/36	15°14.88′	95°00.22′	1.38	1.38	0.75	1.43	11.07	4.60	0.035	0.70	95	0.714517	18.1	0.512113	-10.2	76
SK-175/39	15°14.98′	95°15.16′	0.98	1.61	0.38	1.64	14.24	5.87	0.034	0.85	81	0.717919	22.2	0.512132	-9.9	83
SK-175/41	14°44.84′	95°29.74′	0.75	2.01	0.30	2.05	18.84	6.12	0.039	0.90	70	0.720995	20.6	0.512146	-9.6	86
SK-175/44	15°15.00′	95°45.23′	0.80	1.83	0.32	1.77	16.87	5.56	0.036	0.82	69	0.721241	23.7	0.512091	-10.7	85
SK-175/45	15°30.32′	95°45.30′	0.73	1.81	0.31	1.63	16.18	5.82	0.041	1.01	76	0.721578	23.7	0.512071	-11.1	85
SK-175/46	15°15.00′	95°59.64′	0.90	1.81	0.38	1.54	15.45	5.50	0.038	0.75	78	0.720775	22.7	0.512069	-11.1	83
SK-175/47	15°15.03′	96°14.61′	0.92	1.85	0.38	1.57	15.37	5.77	0.042	0.99	66	0.720946	38.6	0.512102	-10.4	83
SK-175/48	15°15.65′	96°29.81′	0.77	1.88	0.27	1.49	NA	7.25	0.042	0.97	68	0.722994	27.5	0.512087	-10.8	
SK-175/49	15°15.29′	96°45.14′	0.87	1.95	0.32	1.65	16.70	6.07	0.049	0.86	72	0.722443	24.6	0.512053	-11.4	84
SK-175/50	15°14.85′	96°59.65′	0.71	1.56	0.29	1.25	11.87	6.02	0.040	0.82	71	0.723430	25.3	0.512078	-10.9	82
SK-175/51	15°14.55′	97°15.03′	0.75	1.59	0.30	1.30	12.76	6.28	0.052	0.83	70	0.723142	31.1	0.512079	-10.9	83
SK-175/52	15°00.69′	97°15.03′	0.77	1.46	0.42	0.60	5.70	2.70	0.023	0.34	66	0.722788	13.0	0.511959	-13.2	68
SK-175/54	14°59.37′	96°44.76′	0.84	1.74	0.34	1.71	16.02	6.67	0.047	0.80	70	0.722522	22.5	0.512108	-10.3	85
SK-175/55	15°00.04′	96°29.74′	0.82	1.69	0.36	1.64	14.30	6.17	0.042	0.85	73	0.724791	28.7	0.512088	-10.7	83
SK-175/57	15°00.03′	95°59.98′	0.81	1.82	0.39	1.75	16.16	5.95	0.053	0.78	74	0.722000	24.9	0.512092	-10.6	84
SK-175/66	14°30.40′	96°29.73′	0.74	1.93	0.27	1.88	18.07	6.56	0.046	0.88	71	0.722268	24.9	0.512093	-10.6	86
SK-175/69	15°30.50′	96°07.50′	0.94	1.78	0.55	0.82	8.66	2.57	0.029	0.42	80	0.722260	22.4	0.511973	-13.0	73
SK-175/70	15°45.03′	96°09.57′	0.21	0.70	0.11	0.77	5.89	1.78	0.014	0.22	66	0.724474	10.8	0.512082	-10.8	85
SK-175/71	15°39.03′	96°34.58′	0.79	1.86	0.35	1.69	15.79	5.55	0.044	0.74	61	0.721855	23.2	0.512050	-11.5	84
SK-175/72	15°30.29′	96°40.31′	0.75	2.03	0.29	1.72	17.16	6.05	0.039	0.81	66	0.722437	27.7	0.512078	-10.9	85
SK-175/76	14°30.13′	95°30.01′	1.32	1.58	1.05	1.45	11.07	4.17	0.036	0.69	112	0.714620	20.0	0.512054	-11.4	74
SK-175/79	14°00.04′	97°30.14′	0.64	1.16	0.51	0.22	2.64	1.65	0.020	0.55	66	0.724030	17.8	0.511945	-13.5	53
SK-175/80	14°14.99′	97°30.11′	0.66	1.25	0.42	0.27	3.25	1.94	0.022	0.47	67	0.722759	9.0	0.511990	-12.6	58
SK-175/83	14°15.09′	96°45.46′	0.55	1.61	0.24	0.89	9.97	6.97	0.027	0.65	53	0.726911	17.0	0.511973	-13.0	81
SK-175/87	14°15.11′	95°45.12′	1.22	1.65	1.12	1.38	11.56	3.66	0.038	0.98	115	0.716841	22.8	0.512085	-10.8	74
SK-175/94	14°15.28′	94°00.07′	0.97	1.64	0.57	1.78	14.51	4.89	0.036	0.71	87	0.717886	17.2	0.512093	-10.6	82
SK-175/96	14°00.83′	94°29.29′	1.17	1.65	0.84	1.53	13.13	4.07	0.031	0.63	106	0.716333	19.9	0.512066	-11.2	78
SK-175/100	13°46.98′	95°52.00′	0.97	1.94	0.59	1.97	16.19	5.12	0.033	0.70	78	0.721181	22.0	0.512051	-11.5	82
SK-175/103	13°45.06′	96°29.63′	0.74	1.50	0.46	1.03	7.30	4.86	0.033	0.45	65	0.723240	22.5	0.511955	-13.3	73
SK-175/108	13°45.04′	97°45.13′	0.47	1.99	0.27	1.48	15.68	5.45	0.025	0.75	50	0.733000	23.6	0.511880	-14.8	85
SK-175/115	13°00.10′	96°34.59′	0.61	1.89	0.29	1.14	13.19	3.60	0.027	0.74	48	0.732160	26.8	0.511870	-15.0	83
SK-175/118	13°00.43′	98°29.85′	0.17	0.94	0.12	0.39	2.63	1.51	0.010	0.20	17	0.738966	6.8	0.511827	-15.8	68
SK-175/120	12°30.47′	97°30.01′	0.11	0.45	0.09	0.30	0.87	0.67	0.005	0.11	10	0.738400	4.3	0.511753	-17.2	57
SK-175/123	12°15.24′	96°59.84′	0.18	0.75	0.12	0.86	2.56	1.99	0.013	0.41	16	0.742183	16.5	0.511763	-17.1	71
SK-175/129	12°00.25′	96°29.98′	0.92	1.98	1.34	2.34	16.86	6.02	0.039	0.75	65	0.721891	18.7	0.511951	-13.4	80
Yangon R. SPM	16°52.50′	96°05.45′	0.81	1.96	0.47	2.66	22.68	8.66	0.051	1.14	70	0.716716	26.2	0.512171	-9.1	87
Salween R. BL	16°32.05′	97°37.20′	0.88	1.93	0.54	1.23	11.51	4.46	0.029	0.80	70	0.731794	21.3	0.511885	-14.7	77
Salween R. SPM	16°32.00′	97°37.10′	0.96	1.92	0.51	1.15	10.31	4.08	0.027	0.67	72	0.731435	22.9	0.511847	-15.4	75

R, River; BL, Bed load; SPM, Suspended particulate mater, $\varepsilon_{Nd}(0)$: ε_{Nd} at present time, which is expressed as, $\varepsilon_{Nd}(0) = [(^{143}Nd/^{144}Nd)_{Samp.}/(^{143}Nd/^{144}Nd)_{CHUR-1}] \times 10^4$. Whereas, subscript Samp. represents sample and CHUR stands for chondritic uniform reservoir. NA, Not Analyzed.

introduce a part of it. Al in these sediments varies linearly with K, Mg, Fe, and Ti with a correlation coefficient (r for number of samples n = 46) 0.79, 0.86, 0.74, and 0.73 respectively, however, there is a very poor correlation of Al with Na (r = 0.31 for n =46) and Ca (r = 0.01 for n = 46). These correlations could be due to the dominance of ferromagnesian silicates in the source regions followed by weathering and transport causing loss of mobile element sand size sorting. The statistically significant relationship between iron and aluminum suggests that iron oxides are not important since Fe is associated with aluminum in aluminosilicate phases (Alagarsamy et al., 2010). Lack of correlation of Ca and Na with Al in these sediments results from preferential loss of these mobile elements with respect to Al during chemical weathering. Ti is very less abundant but shows a significant positive correlation with Al due to similar source, chemical behavior, and size sorting. K is more abundant in feldspar and illite so that the variations in the K/Al ratio may reflect the variations in feldspar and illite abundances present in the sediments due to inherent source signature or due to weathering and transport. Higher K concentration shows more feldspar and illite (Colin et al., 1999; Singh et al., 2008) in these sediments. On FM-CN-K (Fe₂O₃+ MgO - CaO + Na₂O - K₂O) diagram (**Figure 4A**) a large number of samples plot toward FM apex confirming their ferromagnesian affinity which is further supported by good positive correlation (r = 0.81 for n= 46) between Fe and Mg. Mafic rocks such as basalts/ophiolites present in the drainage of the upper Irrawaddy catchment, in the central trough and in the Indo-Burman-Arakan (IBA) ranges could be an important source of sediments to the Andaman Shelf even though they occupy only small fraction of the Irrawady catchment. On A-CN-K (Al₂O₃ - CaO + Na₂O -K₂O) ternary plot (Figure 4B) the majority of samples of the Andaman Shelf plot parallel to A-CN join, indicating progressive chemical weathering of the samples originating from mafic compositions. Variable chemical weathering of these sediments is also reflected by their variable Chemical Index of Alteration $(CIA = [Al_2O_3/(Na_2O + K_2O + CaO + Al_2O_3)] \times 100; Nesbitt$ and Young, 1982). CIA values of the Andaman Shelf sediments range between 53 and 88% (Table 1), suggesting significant variation in their chemical weathering. Few samples collected around the Mergui Shelf region contain very low concentrations of all the major elements analyzed in this study; this could be due to the fact that they are coarse-grained sands (Rodolfo, 1969) mostly dominated by quartz.

Provenance Tracing Using Sr and Nd Isotopic Systematics

Sr and Nd concentrations and their isotope compositions in the Andaman Shelf sediments were analyzed in their silicate phases. $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios in these sediments show significant variations, ranging between 0.712245 and 0.742183. Their Sr concentrations lie between 10 and 162 μ g/g. Nd concentrations and $\epsilon_{\rm Nd}(0)$ in these shelf sediments vary from 2.4 to 38.6 μ g/g and -6.29 to -17.25 respectively. $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios of surface-slurry and bank sediments at the mouth of the Salween River are 0.731794 and 0.731435 with Sr concentrations, 70 and 72 μ g/g and their

 $\varepsilon_{\rm Nd}(0)$ are -14.69 and -15.43 with Nd concentrations, 21.3 and 22.9 μ g/g respectively. Sediment collected at the mouth of the Yangon River, a distributary of the Irrawaddy River has ⁸⁷Sr/⁸⁶Sr ratios and $\varepsilon_{Nd}(0)$ 0.716716 and -9.11 with their Sr and Nd concentrations 70 and 26.2 µg/g respectively. Majority of the samples from the Andaman Shelf have ⁸⁷Sr/⁸⁶Sr ratios between 0.712245 and 0.733000 and $\epsilon_{Nd}(0), \ -9.11$ and -15.43 with Sr and Nd concentrations around 75 μ g/g and 25 μ g/g respectively. Few samples collected close to Arakan Coast have lower 87 Sr/86 Sr ratios, 0.716734–0.713101 and higher radiogenic Nd, $\varepsilon_{Nd}(0)$ values -6.29 to -7.21 respectively, reflecting their Indo-Burman ranges association (Licht et al., 2013). A few samples collected close to Mergui Archipelago have high radiogenic 87 Sr/86 Sr ratios, 0.738400-0.742183 and low $\varepsilon_{Nd}(0)$, -15.82 to -17.25. These radiogenic Sr and non-radiogenic Nd are similar to those reported for the sediments of delta region of the Lower Meghna (combined G-B; Galy and France-Lanord, 2001), however, it is quite unlikely to get G-B sediments at this location, this region being very far from the G-B reaches and lying away from their sediment transport pathways.

 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and ϵ_{Nd} of sediments from the various river and ocean basins have been used successfully to track their sources (Goldstein and O'Nions, 1981; Bouquillon et al., 1990; France-Lanord et al., 1993; Galy et al., 1996, 2010; Winter et al., 1997; Pierson-Wickmann et al., 2001; Clift et al., 2002; Singh and France-Lanord, 2002; Banner, 2004; Ahmad et al., 2005, 2009; Colin et al., 2006; Singh et al., 2008; Viers et al., 2008; Rahaman et al., 2011; Tripathy et al., 2011; Goswami et al., 2012; Awasthi et al., 2014; Ali et al., 2015). These isotope pairs are used as reliable proxies to track the sediment sources, as there are distinct differences in their composition in the different lithologies supplying these sediments. However, successful tracking of the sediment sources using Sr-Nd isotope pair depends to a great extent on their preservation during their weathering and transport. Weathering and transport of the sediments may influence the isotope composition of Sr compared to that of Nd due to mobile nature of the former, making the Nd isotope composition more robust provenance tracer (Walter et al., 2000; Tutken et al., 2002). Robustness of Sr and Nd isotope compositions in tracking the sediment sources in the Andaman Shelf can be verified by observing their relation with Al and chemical index of alteration (CIA) as they get influenced by the processes of size sorting and chemical weathering respectively which might affect the isotope composition of Sr and Nd of these sediments (Singh et al., 2008). 87 Sr/ 86 Sr and ϵ_{Nd} of the sediments of Andaman Shelf have been plotted with their Al contents and CIA in Figures 5A-D. These scatter plots do not show any interrelation among Sr-Nd isotope composition, Al contents and CIA of the sediments, suggesting the minimal influence of weathering and transport on these isotope compositions and hence they can be used quite reliably to track the sources of these sediments.

Figures 6A,B shows the distribution patterns of ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios and ϵ_{Nd} in the Andaman Shelf. These distribution patterns show three distinct zones with their characteristic Sr-Nd isotope signatures. The first zone, comprising the Western Myanmar Shelf region along Arakan Coast and around the mouth of the







Irrawaddy River, is characterized by lower ⁸⁷Sr/⁸⁶Sr and higher ϵ_{Nd} . This zone probably gets sediments through Kaladan, Naf and other smaller rivers draining the IBA ranges having ⁸⁷Sr/⁸⁶Sr ratios, 0.714 - 0.718 and $\varepsilon_{Nd}(0)$, -7.8--3.9 (Licht et al., 2013) and through Irrawaddy Rivers. The second zone is the area around the mouth of the Salween River with higher ⁸⁷Sr/⁸⁶Sr and lower ϵ_{Nd} and gets sediments from the Salween River. The third zone is characterized by distinctly high ⁸⁷Sr/⁸⁶Sr and low ε_{Nd} around the Mergui Archipelago in the Southern Myanmar. The Sr-Nd isotope compositions of these sediments is very similar to those of the Lower Meghna (Galy and France-Lanord, 2001). The sediments from the GBR system may come to the Andaman Shelf and to the Mergui Archipelago region through the North/South Preparis Channel. It is, however, very difficult to envisage GBR sediments reaching such far a location without impacting the sediments of shelf region around the mouth of the Irrawaddy. Eastern Andaman Shelf sediments do not show affinity with those from the Irrawaddy and the Salween Rivers either. These sediments, therefore, require another source. Close inspection of lithologies around the Mergui Archipelago and very few available isotope data for them suggest that the granites from the Central and Western belts with higher ⁸⁷Sr/⁸⁶Sr and lower ε_{Nd} (Nakapadungrat et al., 1984; Liew and McCulloch, 1985) present in the Southern Myanmar and Western Thailand could be the possible source of these sediments. The Tanintharyi, Tavoy and other smaller rivers flowing these granitic belts could possibly be bringing sediments around the Mergui Archipelago. Part of sediments in this region might originate from the erosion of several small islands of the Mergui Archipelago itself. Granites of the Southern Myanmar and Western Thailand were not known to be a major source of sediments to the Andaman Shelf earlier. This study however, identifies these granitic belts as an important source of sediments to the Eastern Andaman Shelf in Southern Myanmar.

To further identify the sources of sediments of the Andaman Shelf, their Sr and Nd isotope compositions have been plotted on two isotopes mixing diagram (Figure 7). There could be five potential sources of sediments of the Andaman Shelf: (i) Rivers draining the IBA Ranges with low 87 Sr/86 Sr and high $\varepsilon_{\rm Nd}$, (ii) Irrawaddy River with low ${}^{87}{\rm Sr}/{}^{86}{\rm Sr}$ and high $\varepsilon_{\rm Nd}$, (iii) Salween River with higher 87 Sr/ 86 Sr and low ε_{Nd} , (iv) G-B river system with high 87 Sr/86 Sr and low ENdand (v) Rivers draining the Southern Myanmar and Western Thailand with high 87 Sr/ 86 Sr and low ϵ_{Nd} . The Sr and Nd isotope compositions of the possible dominant end-members (Table 2) are also plotted. The isotope compositions of these end-members (Table 2) are assigned based on those available in the literatures and based on few samples of the Irrawaddy and the Salween Rivers analyzed this study. Due to lack of study in Myanmar and adjoining areas, isotope values of some of the end-members need to be fixed







Andaman Shelf are derived from the Irrawaddy river along with the Salween and rivers flowing through the western slopes of the Indo–Burman–Arakan and Western/Central granitic ranges. Blue curve represents the hyperbolic two end member mixing curve where as ticks on them indicate the fractions of the end members.

either using the few available data or indirectly. There is no data available on the smaller rivers flowing through the western slopes of the IBA ranges along the Arakan Coast. Sr-Nd isotope compositions for the lithologies present in Indo-Burman ranges (Licht et al., 2013) have been considered for these rivers (Colin et al., 1999). Sr, Nd isotope compositions of two sediment samples of unknown locations of the Irrawaddy River is available in the literature (Colin et al., 1999; Allen et al., 2008). In this study, one sediment sample from the mouth of the Yangon, one of the distributaries of the Irrawaddy River, was analyzed for its Sr and Nd isotope compositions which are consistent with the earlier reported values. Irrawaddy end-member is based on these three data (Table 2). The Salween end-member is characterized by Sr and Nd isotope composition of two sediment samples collected from its mouth and analyzed in this study (Table 2). The Sr isotope value of this end-member is supported by high ⁸⁷Sr/⁸⁶Sr observed in granites present in its catchment (Nakapadungrat et al., 1984). Fixing the end-member values for sediments brought by the Tanintharyi, the Tavoy and other smaller rivers in Southern Myanmar was difficult as these rivers have never been analyzed and data are not available. As these rivers mostly flow through the Western/Central granitic belts (Figure 2), the few data available on these granites on Sr and Nd isotopes from the Southern Myanmar and Western Thailand (Nakapadungrat et al., 1984; Liew and McCulloch, 1985) have been used to constrain this end-member (Table 2). The end-member values of the Ganga-Brahmaputra River is based on the data of the Lower Meghna (Galy and France-Lanord, 2001).

On the Sr-Nd isotope mixing diagram (**Figure 7**), samples collected from the shelf area along Arakan Coast show an affinity toward IBA end-member suggesting that the rivers such as the

Kaladan, Naf and other small rivers flowing through the Arakan Coast deliver sediment to the near by shelf. Impact of the G-B river system on the Western Myanmar Shelf sediments seems to be quite minimal, if any, despite their proximity with the G-B delta. The eastward surface current flowing from the G-B delta toward this shelf is unable to bring an appreciable amount of sediments from the G-B delta to the Western Myanmar Shelf. Sr and Nd isotope composition of several samples plot near the Irrawaddy end-member suggest that this river is the major source of sediments to the Andaman Shelf. Sediments from the Gulf of Martban are a mixture of sediments derived from the Irrawaddy and the Salween Rivers in more or less an equal proportion. Further south-east, near the mouth of the Tavoy River, sediments of the Irrawaddy origin are still present, though in lesser fraction compared to the Gulf of Martban. Sediments from the shelf around the South Myanmar are quite unique. They have high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $\epsilon_{Nd},$ similar to those from the G-B river system in the Bangladesh. As discussed above, G-B sediments cannot reach near the Mergui Archipelago and majority of these sediments are derived from the erosion of the granitic belts from the Southern Myanmar and Western Thailand. These are a mixture of sediments derived from the Tanintharyi, the Irrawaddy, and the Salween Rivers. It is almost clear from Figures 6, 7 that G-B river system contributes very little sediments to the Andaman Shelf. It is unlikely that Bengal shelf sediments are reaching the Andaman Shelf in recent times

Control on Erosion Determining the Sediment Sources

It is borne out from the above discussion that majority of the sediments in the Andaman Shelf are derived from (i) the Irrawaddy River, (ii) the Salween River, (iii) IBA ranges through the rivers of the Arakan Coast and (iv) Central and Western granite belts in the Southern Myanmar and Western Thailand through the Tavoy, the Tanintharyi and other smaller rivers (Figure 1). Large sediment supply from the IBA ranges through smaller rivers of western slopes of the IBA and through the Irrawaddy and Southern/Western granitic belts suggest significantly higher erosion rates over them. Observation of high erosion over the IBA ranges was suggested earlier by Colin et al. (1999). However, high erosion over the Western/Central granitic belt is reported for the first time in this study. Higher erosion over these two ranges seems to be controlled by the intense and focussed precipitation and topography (relief). Annual rainfall over the IBA and Western/Central granite ranges is as high as 5 m (Figure 2), much higher compared to other regions providing sediments to the Andaman Shelf. Most of this rainfall occurs during the south-west monsoon. Further, the high and focussed precipitation coincides with higher relief on western slopes (Figure 8) of these ranges. Rainfall and elevation along the transects following the SW monsoon tracks, two over the IBA and one over the Southern/Western granite ranges are plotted in the Figure 8. Along all these sections, high and focussed precipitation coincides with higher relief along the western slopes of these ranges causing higher stream power

TABLE 2	The end-members	of Northern	Andaman Sh	elf sediments.	with their	isotopic r	properties
		••••••••••••					

End-member	⁸⁷ Sr/ ⁸⁶ Sr	⁸⁷ Sr/ ⁸⁶ Sr Mean (SD)	εNd	ε _{Nd} Mean (SD)	References
Ganga–Brahmaputra	0.7379–0.7530	0.7455 (0.0107)	-14.8 to -17.4	-16.1 (1.8)	Galy and France-Lanord, 2001
Indo-Burman-Arakan	0.7050-0.7180	0.7101 (0.0037)	0.3 to -8.0	-5.2 (2.7)	Colin et al., 1999; Allen et al., 2008; Najman et al., 2008; Licht et al., 2013
Irrawaddy River	0.7080-0.7135	0.7129 (0.0031)	-8.3 to -12.2	-10.3 (1.6)	Colin et al., 1999; Allen et al., 2008; Present Study
Salween River	0.7314–0.7318	0.7316 (0.0003)	-14.7 to -15.4	-15.1 (0.5)	Present study
Southern Myanmar/Western Thailand	0.7256-0.8272	0.7685 (0.0264)	-23.0 to -27.3	-25.4 (1.5)	Nakapadungrat et al., 1984; Liew and McCulloch, 1985



precipitations over the higher relief of the western slopes of the IBA (Transects AA', BB') and Western/Central granitic ranges (Transect CC') cause higher erosion in these catchment (Source: http://dwtkns.com/srtm/ and http://trmm.gsfc.nasa.gov/).

leading to higher erosion. Such higher erosion due to focussed precipitation on higher relief on the southern slopes of the Higher Himalaya has been reported earlier too (Singh and France-Lanord, 2002; Hodges et al., 2004; Thiede et al., 2004; Wobus et al., 2005; Singh, 2006; Singh et al., 2008). Thus, the sediment budget of the Andaman Shelf, in addition to the Himalayan– Tibetan ranges, is controlled by erosion over the Indo–Burman– Arakan and Western/Central granitic ranges due to intense and focussed precipitation over the higher relief of their western slopes.

Role of Sea-Surface Current in Controlling the Sediment Dispersion

The sea-surface current of the Andaman sea observes two reversal. It flows eastward during SW monsoon and westward during NE monsoon (**Figure 1**). As most of the precipitation occur during the south-west monsoon causing higher erosion leading to \sim 90% of annual sediment discharge, therefore eastward current from the BoB and from the shelf along the Arakan Coast brings sediments to the Northern Andaman Shelf which mix with sediment brought by the Irrawaddy River and get deposited on the shelf. These sediments get transported further eastward and mix with sediments from the Salween and get deposited in Gulf of Martban and on the eastern shelf (Figure 1). These currents bring sediments from the Irrawaddy and the Salween Rivers further to the south which get deposited after mixing with sediments brought by the Tavoy and the Taninthrayi Rivers. During the north-east monsoon the sea-surface current in the Andaman Sea reverses and flows westward (Figure 1). However, low precipitation during NE monsoon leads to less erosion in the catchment and hence lower sediment delivery to the shelf. Part of the sediments deposited on this shelf during SW monsoon get transported westward to the Eastern BoB during NE monsoon (Colin et al., 1999; Ramaswamy et al., 2004).

CONCLUSION

Major element and Sr and Nd concentrations and their isotope compositions have been determined in the silicate fraction of the sediments deposited on the Northern and Eastern Andaman Shelf to constrain their sources and factors influencing their erosion, dispersal, and deposition. Major element compositions of the majority of these sediments indicate their ferromagnesian nature which is sourced from mafic lithologies present in the drainage of the Irrawaddy River and over the IBA. Sr and Nd isotope compositions of Andaman Shelf sediments suggest that these sediments are mostly derived from (i) the Irrawaddy River,

REFERENCES

- Ahmad, S. M., Anil Babu, G., Padmakumari, V. M., Dayal, A. M., Sukhija, B. S., and Nagabhushanam, P. (2005). Sr, Nd isotopic evidence of terrigenous flux variations in the Bay of Bengal: implications of monsoons during the last ~34,000 years. *Geophys. Res. Lett.* 32:L22711. doi: 10.1029/2005GL 024519
- Ahmad, S. M., Padmakumari, V. M., and Anil Babu, G. (2009). Strontium and neodymium isotopic compositions in sediments from Godavari, Krishna and Pennar rivers. *Curr. Sci.* 97, 1766–1769.
- Alagarsamy, R., You, C.-F., Nath, B. N., and Sijin Kumar, A. V. (2010). Determination of rare earth, major and trace elements in authigenic fraction of Andaman Sea (Northeastern Indian Ocean) sediments by Inductively Coupled Plasma-Mass Spectrometry. *Microchem. J.* 94, 90–97. doi: 10.1016/j.microc.2009.09.007
- Ali, S., Hathorne, E. C., Frank, M., Gebregiorgis, D., Stattegger, K., Stumpf, R., et al. (2015). South Asian monsoon history over the past 60 kyr recorded by radiogenic isotopes and clay mineral assemblages in the Andaman Sea. *Geochem.Geophys. Geosyst.* 16, 505–521. doi: 10.1002/2014GC 005586
- Allen, R., Najman, Y., Carter, A., Barfod, D., Bickle, M. J., Chapman, H. J., et al. (2008). Provenance of the Tertiary sedimentary rocks of the Indo-Burman Ranges, Burma (Myanmar): Burman arc or Himalayanderived? J. Geol. Soc. Lond. 165, 1045–1057. doi: 10.1144/0016-764920 07-143
- Awasthi, N., Ray, J. S., Singh, A. K., Band, S. T., and Rai, V. K. (2014). Provenance of the Late Quaternary sediments in the Andaman Sea: implications for

(ii) the Salween River, (iii) the IBA ranges either through the smaller rivers flowing through the Arakan coast or through the Irrawaddy River whose western tributaries such as the Chindwin etc. draining these ranges and (iv) the Western/Central granitic belts of the Myanmar and Thailand through the Tavoy, the Tanintharyi and other smaller rivers. The erosion and sediment delivery from these sources are controlled by the intense and focussed precipitation over the high relief on the western slopes of these ranges and further dispersed by the eastward sea-surface current controlled by SW monsoon on the Northern and Eastern Andaman Shelf. This study for the first time recognizes the higher erosion on the western slopes of the Southern Myanmar, supplying a significant amount of sediment to the Eastern Andaman Shelf around the Mergui Archipelago.

AUTHOR CONTRIBUTIONS

SS and KD planned the experiment wrote the manuscript. VR and PR collected the samples. KD conducted the experiments and VR helped in isotope measurements. All authors contributed in interpreting the data.

ACKNOWLEDGMENTS

KD thanks Ravikant Prasad and Mithun M. for their help in refining DEM and precipitation figures. We sincerely thank Selvaraj Kandasamy, the associate editor for his positive feedback on this manuscript. Detailed reviews of Liviu Giosan, Ludvig Löwemark and Armstrong-Altrin John S. helped improve this manuscript considerably.

monsoon variability and ocean circulation. Geochem. Geophys. Geosyst. 15, 3890–3906. doi: 10.1002/2014GC005462

- Banner, J. L. (2004). Radiogenic isotopes: systematics and applications to earth surfaceprocesses and chemical stratigraphy. *Earth Sci. Rev.* 65, 141–194. doi: 10.1016/S0012-8252(03)00086-2
- Bird, M. I., Robinson, R. A. J., Oo, N. W., Aye, M. M., Lud, X. X., Higgitt, D. L., et al. (2008). A preliminary estimate of organic carbon transport by the Ayeyarwady (Irrawaddy) and Thanlwin (Salween) Rivers of Myanmar. *Quat. Int.* 186, 113–122. doi: 10.1016/j.quaint.2007.08.003
- Bouquillon, A., France-Lanord, C., Michard, A., and Tiercelin, J. J. (1990). Sedimentology and isotopic chemistry of the Bengal fansediments: the denudation of the Himalaya. *Proc. Ocean Drill. Prog. Sci. Results* 116, 43–58.
- Chapman, H., Bickle, M., Thaw, S. H., and Thiam, H. N. (2015). Chemical fluxes from time series sampling of the Irrawaddy and Salween Rivers, Myanmar. *Chem. Geol.* 401, 15–27. doi: 10.1016/j.chemgeo.2015. 02.012
- Clift, P. D., Lee, J. I., Hildebrand, P., Shimizu, N., Layne, G. D., Blusztajn, J., et al. (2002). Nd and Pb isotope variability in the Indus River system: Implicationsfor sediment provenance and crustal heterogeneity in theWestern Himalaya. *Earth Planet. Sci. Lett.* 200, 91–106. doi: 10.1016/S0012-821X(02) 00620-9
- Colin, C., Turpin, L., Bertaux, J., Desprairies, A., and Kissel, C. (1999). Erosional history of the Himalayan and Burman ranges duringthe last two glacialinterglacial cycles. *Earth Planet. Sci. Lett.* 171, 647–660. doi: 10.1016/S0012-821X(99)00184-3
- Colin, C., Turpin, L., Blamart, D., Frank, N., Kissel, C., and Duchamp, S. (2006). Evolution of weathering patterns in the Indo-Burman Ranges

over the last 280 kyr: effects of sediment provenance on 87Sr/86Sr ratios tracer. *Geochem. Geophys. Geosyst.* 7:Q03007. doi: 10.1029/2005GC 000962

- Darbyshire, D. P. F., and Swainbank, I. G. (1988). Geochronology of a Selection of Granites from Burma. NERC Isotope Geology Centre Report 88/006.
- France-Lanord, C., Deny, L. A., and Michard, A. (1993). Evolution of the Himalaya since Miocene time: isotopic and sedimentological evidence from the Bengal Fan. Himalayan Tectonic. *Geol. Soc. Spec. Pub.* 74, 603–621. doi: 10.1144/GSL.SP.1993.074.01.40
- France-Lanord, C., and Derry, L. A. (1997). Organic carbon burial forcing of the carbon cycle from Himalayan erosion. *Nature* 390, 65–67. doi: 10.1038/36324
- Galy, A., and France-Lanord, C. (2001). Higher erosion rates in the Himalaya: Geochemical constraintson riverine fluxes. *Geology* 29, 23–26. doi: 10.1130/ 0091-7613(2001)029%3C0023:HERITH%3E2.0.CO;2
- Galy, A., France-Lanord, C., and Deny, L. A. (1996). Oligo-Miocène uplift and unroofing of the Himalaya: evidence from the Bengal Fan. *Tectonophysics* 260, 109–118. doi: 10.1016/0040-1951(96)00079-0
- Galy, V., France-Lanord, C., Peucker-Ehrenbrink, B., and Huyghe, P. (2010). Sr-Nd-Osevidence for a stable erosion regime in the Himalaya during thepast 12 Myr. *Earth Planet. Sci. Lett.* 290, 474–480. doi: 10.1016/j.epsl.2010. 01.004
- Goldstein, S. L., O'Nions, R. K., and Hamilton, P. J. (1984). ASm-Nd isotopic study of atmospheric dusts and particulatesfrom major river systems. *Earth Planet. Sci. Lett.* 70, 221–236.
- Goldstein, S. L., and O'Nions, R. K. (1981). Nd and Sr isotopic relationships in pelagic clays and ferromanganese deposits.*Nature* 292, 324–327. doi: 10.1038/292324a0
- Goswami, V., Singh, S. K., Bhushan, R., and Rai, V. K. (2012). Temporal variations in 87Sr/86Sr and $\epsilon_{\rm Nd}$ in sediments of the southeastern Arabian Sea: impact of monsoonand surfacewater circulation. *Geochem. Geophys. Geosyst.* 13:Q01001. doi: 10.1029/2011GC003802
- Hodges, K. V., Wobus, C., Ruhl, K., Schildgen, T., and Whipple, K. (2004). Quaternary deformation, river steepening, and heavy precipitation at the front of the Higher Himalayan ranges. *Earth Planet. Sci. Lett.* 220, 379–389. doi: 10.1016/S0012-821X(04)00063-9
- Licht, A., France-Lanord, C., Reisberg, L., Fontaine, C., Soe, A. N., and Jaeger, J.-J. (2013). A palaeo Tibet-Myanmar connection? Reconstructing the Late Eocene drainage system of central Myanmar using a multi-proxy approach. J. Geol. Soc. Lond. 170, 929–939. doi: 10.1144/jgs2012-126
- Liew, T. C., and McCulloch, M. T. (1985). Genesis of granitoid batholiths of Peninsular Malaysiaand implications for models of crustal evolution: evidence from aNd-Sr isotopic and U-PI, zircon study. *Geochim. Cosmochim. Acta* 49, 587–600. doi: 10.1016/0016-7037(85)90050-X
- Maury, R. C., Pubellier, M., Rangin, C., Wulput, L., Cotten, J., Socquet, A., et al. (2004). Quaternary calc-alkaline and alkaline volcanism inan hyper-oblique convergence setting, central Myanmar and western Yunnan. *Bull. Soc. Géol. France* 175, 461–472. doi: 10.2113/175.5.461
- Najman, Y., Johnson, C., White, N. M., and Oliver, G. (2004). Evolution of the Himalayan foreland basin, NW India. *Basin Res.* 16, 1–24. doi: 10.1111/j.1365-2117.2004.00223.x
- Najman, Y., Bickle, M., BouDagher-Fadel, M., Cater, A., Garzanti, E., Paul, M., et al. (2008). The Paleogene record of Himalayan erosion: Bengal Basin, Bangladesh. *Earth Planet. Sci. Lett.* 273, 1–14. doi: 10.1016/j.epsl.2008. 04.028
- Nakapadungrat, S., Beckinsale, R. D., and Suensilpong, S. (1984). "Geochronology and geology of Thai granites," in *Proceedings of the Conference on Applications* of Geology and the National Development: Chulalongkorn University (Bangkok), 75–93.
- Nesbitt, H. W., and Young, G. M. (1982). Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature* 299, 715–717. doi: 10.1038/299715a0
- Pierson-Wickmann, A.-C., Reisberg, L., France-Lanord, C., and Kudrass, H. R. (2001). Os-Sr-Nd results from sediments in the Bay of Bengal: implications for sedimenttransport and the marine Os record. *Paleoceanography* 16, 435–444. doi: 10.1029/2000PA000532
- Potemra, J. T., Luther, M. E., and O'Brien, J. J. (1991). The seasonal circulation of theupper ocean in the Bay of Bengal. J. Geophys. Res. 96, 12667–12683. doi: 10.1029/91JC01045

- Potts, P. J. (1992). A Handbook of Silicate Rock Analysis. Milton Keynes: Blackie & Son Ltd. doi: 10.1007/978-1-4615-3270-5
- Rahaman, W., Singh, S. K., and Rajiv, S., and Tandon, S. K. (2011). Sr, C and O isotopes in carbonate nodules from the Ganga Plain: evidence for recentabrupt rise in dissolved ⁸⁷Sr/⁸⁶Sr ratios of the Ganga. *Chem. Geol.* 285, 184–193. doi: 10.1016/j.chemgeo.2011.04.003
- Ramaswamy, V., Gaye, B., Shirodkar, P. V., Rao, P. S., Chivas, A. R., Wheeler, D., et al. (2008). Distribution and sources of organic carbon, nitrogen and their isotopicsignatures in sediments from the Ayeyarwady (Irrawaddy) continental shelf, northern Andaman Sea. *Mar. Chem.* 111, 137–150. doi: 10.1016/j.marchem.2008.04.006
- Ramaswamy, V., Rao, P. S., Rao, K. H., Thwin, S., Rao, N. S., and Raiker, V. (2004). Tidalinfluence on suspended sediment distribution and dispersal in the northern Andaman Seaand Gulf of Martaban. *Mar. Geol.* 208, 33–42. doi: 10.1016/j.margeo.2004.04.019
- Rao, P. S., Ramaswamy, V., and Thwin, S. (2005). Sediment texture, distribution and transporton the Ayeyarwady continental shelf, Andaman Sea. *Mar. Geol.* 216, 239–247. doi: 10.1016/j.margeo.2005.02.016
- Robinson, R. A. J., Bird, M. I., Oo, N. W., Hoey, T. B., Aye, M. M., Higgitt, D. L., et al. (2007). The Irrawaddy River Sediment Flux to the IndianOcean: the Original Nineteenth-century data revisited. J. Geol. 115, 629–640. doi: 10.1086/521607
- Rodolfo, K. S. (1969). Sediments of the Andaman Basin, northeastern Indian Ocean. *Mar. Geol.* 7, 371–402. doi: 10.1016/0025-3227(69) 90014-0
- Singh, S. K. (2006). Spatial variability in erosion in the Brahmaputra basin: causes and impacts. *Curr. Sci.* 90, 1272–1276.
- Singh, S. K., and France-Lanord, C. (2002). Tracing the distribution oferosion in the Brahmaputra watershed from isotopic compositionsof stream sediments. *Earth Planet. Sci. Lett.* 202, 645–662. doi: 10.1016/S0012-821X(02) 00822-1
- Singh, S. K., Rai, S. K., and Krishnaswami, S. (2008). Sr and Nd isotopes in River sediments from theGanga basin: sediment provenance and spatial variability in physical erosion. J. Geophys. Res. 113:F03006. doi: 10.1029/2007JF000909
- Stephenson, D., and Marshall, T. R. (1984). The petrology and mineralogy of Mt. Popa Volcano and the nature of the late-Cenozoic Burma Volcanic Arc. J. Geol. Soc. 141, 747–762. doi: 10.1144/gsjgs.141.4.0747
- Szulc, A. G., Najman, Y., Sinclair, H. D., Pringle, M., Bickle, M., Chapman, H., et al. (2006). Tectonic evolution of the Himalaya constrained by detrital Ar-40–Ar-39, Sm–Nd and petrographic datafrom the Siwalik foreland basin succession, SW Nepal. *Basin Res.* 18, 375–391. doi: 10.1111/j.1365-2117.2006. 00307.x
- Taylor, S. R., and McLennan, S. M. (1985). *The Continental Crust: Its Composition and Evolution*. Carlton: Blackwell Scientific Publication.
- Thiede, R. C., Bookhagen, B., Arrowsmith, J. R., Sobel, E., and Strecker, M. (2004). Climatic control on rapid exhumation along theSouthern Himalayan front. *Earth Planet. Sci. Lett.* 222, 791–806. doi: 10.1016/j.epsl.2004. 03.015
- Tripathy, G. R., Singh, S. K., Bhushan, R., and Ramaswamy, V. (2011). Sr-Nd isotope composition of the Bay of Bengalsediments: impact of climate on erosion in the Himalaya. *Geochem. J.* 45, 175–186. doi: 10.2343/geochemj.1.0112
- Tutken, T., Eisenhauer, A., Wiegand, B., and Hansen, B. T. (2002). Glacialinterglacial cycles in Sr and Nd isotopic composition of Arctic marine sediments triggered by the Svalbard/barents Sea ice sheet. *Mar. Geol.* 182, 351–372. doi: 10.1016/S0025-3227(01)00248-1
- Viers, J., Roddaz, M., Filizola, N., Jean-Loup, G., Sondag, F., Brunet, P., et al. (2008). Seasonal and provenance controls on Nd–Sr isotopic compositions of Amazon riverssuspended sediments and implications for Nd and Sr fluxes exported to the Atlantic Ocean. *Earth Planet. Sci. Lett.* 274, 511–523. doi: 10.1016/j.epsl.2008.08.011
- Walter, H. J., Hegner, E., Diekmann, B., Kuhn, G., Rutgers, V. D., and Loeff, M. M. (2000). Provenance and transport ofterrigenous sediment in the South Atlantic Ocean and theirrelations to glacial and interglacial cycles: Nd and Srisotopic evidence. *Geochim. Cosmochim. Acta* 64, 3813–3827. doi: 10.1016/S0016-7037(00)00476-2
- Win, S. H. (2011). Sediment Dynamics in Irrawaddy River, Myanmar. [The Degree of Masters of Social Sciences]. Singapore: National University of Singapore.

- Winter, B. L., Johnson, C. L., and Clark, D. L. (1997). Strontium, neodymium and lead isotope variations of authigenic andsilicate sediment components from the Late Cenozoic Arctic Ocean: implications for sediment provenance and source oftrace metals in sea water. *Geochim. Cosmochim. Acta* 61, 4181–4200. doi: 10.1016/S0016-7037(97) 00215-9
- Wobus, C., Heimsath, A., Whipple, K., and Hodges, K. (2005). Active outof-sequence thrust faulting in the central Nepalese Himalaya. *Nature* 434, 1008–1011. doi: 10.1038/nature03499
- Wyrtki, K. (1973). "Physical oceanography of the Indian Ocean," in *The biology of the Indian Ocean*, ed B. Zietschel (New York, NY: Springer), 18–36.

Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Copyright © 2016 Damodararao, Singh, Rai, Ramaswamy and Rao. This is an openaccess article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) or licensor are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.