Concentration of Heavy metals in the food chain components of the near shore coastal waters of Kalpakkam, South East Coast of India, Bay of Bengal

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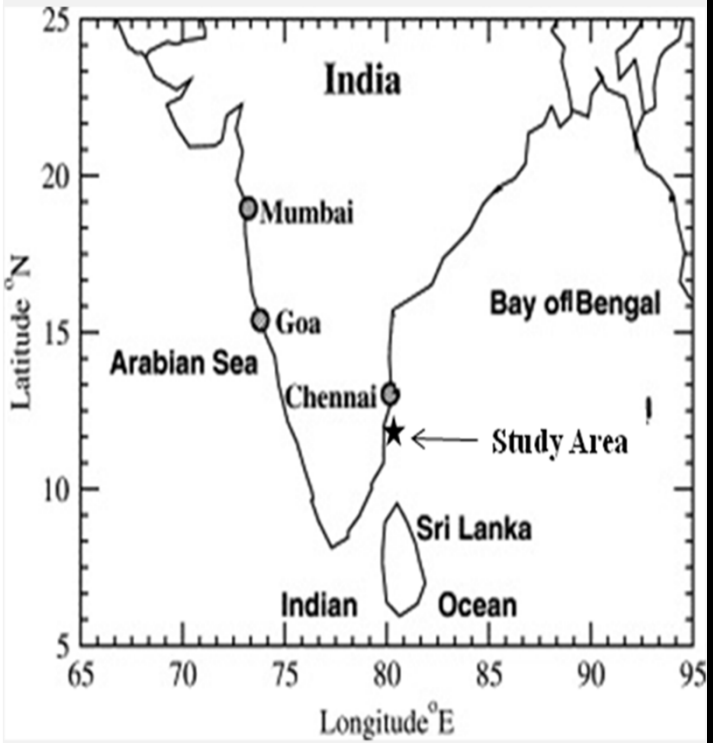
Objective:

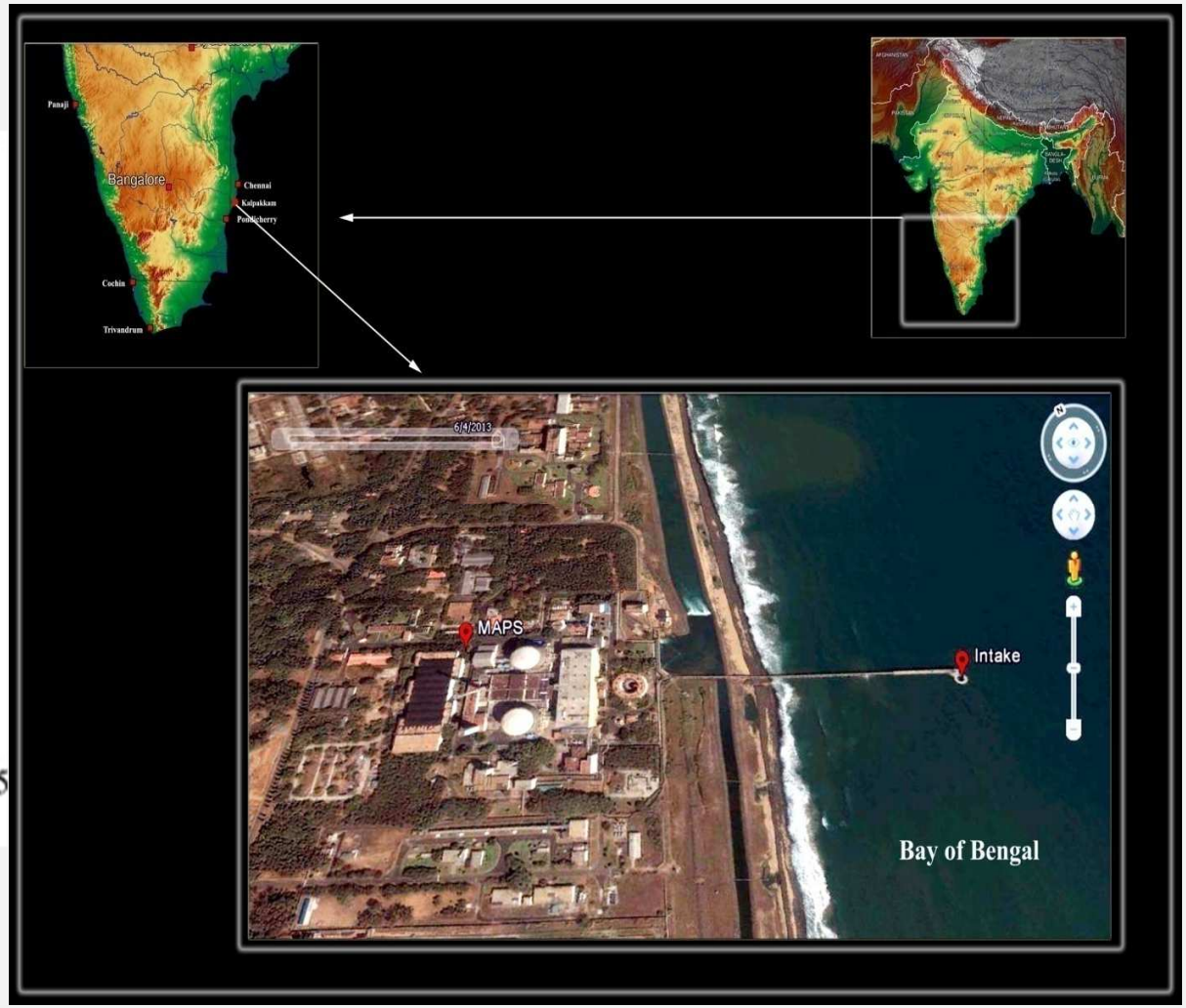
- To assess the concentration of heavy metals (Fe, Zn, Pb, Cu, Mn, Cr & Cd) in different food web components such as water, sediment, zooplankton and fish in the near shore waters of Kalpakkam

- To understand their pattern of distribution

- To estimate Bioaccumulation Factor

Study area showing the station location





Nuclear facilities at Kalpakkam

(12° 33' N Lat. and 80° 11' E Long.)

- IGCAR
- FBTR
- MAPS
- KARP
- NDDP
- BHAVINI/ PFBR
- PRP

IGCAR

MAPS

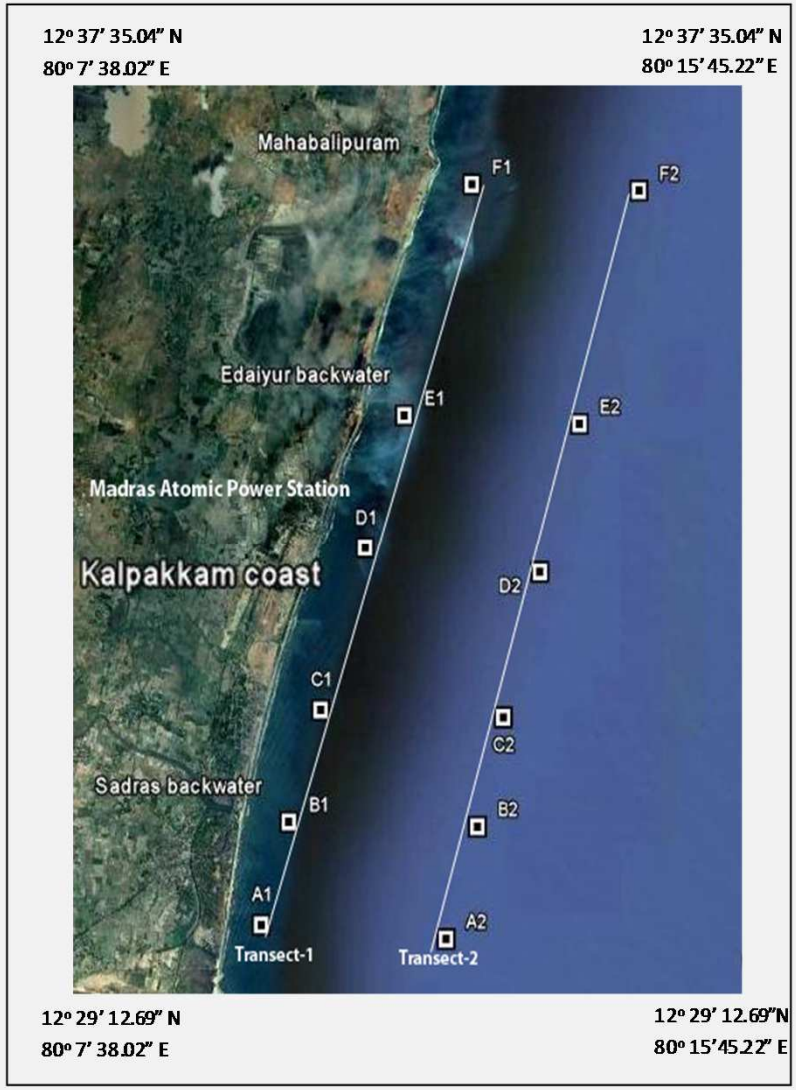
KARP

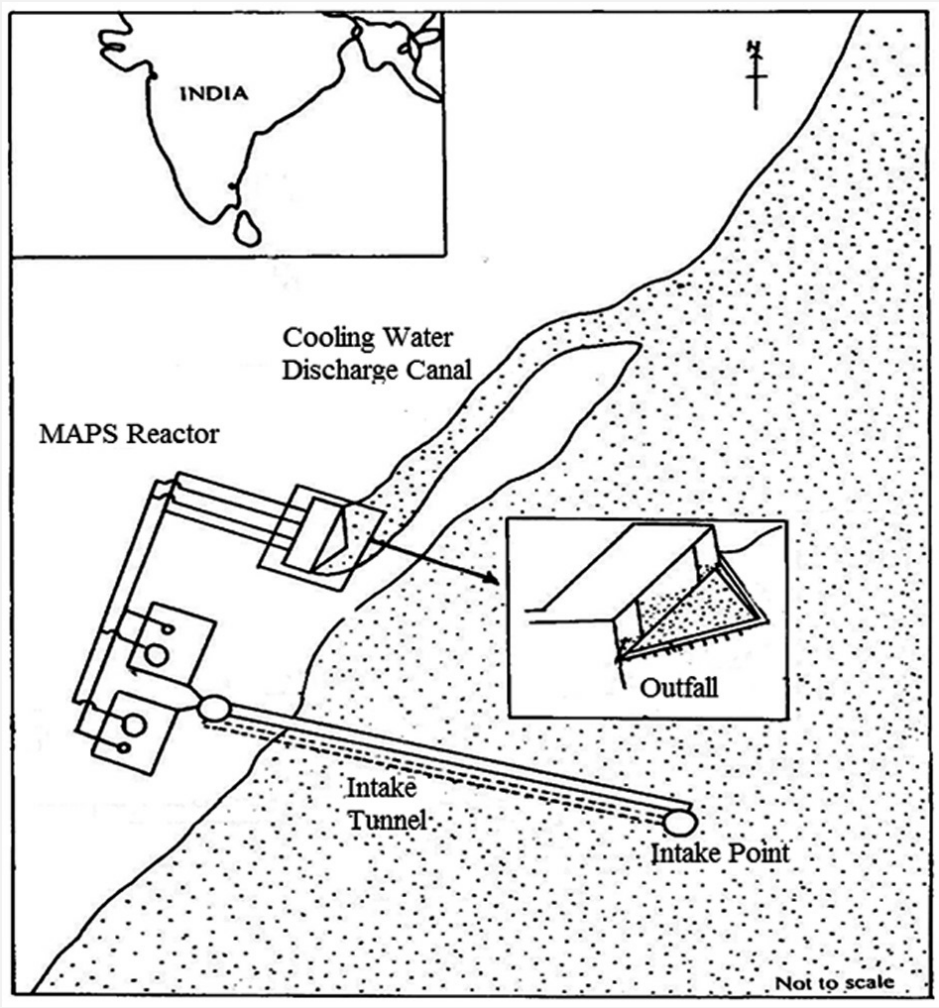
NDDP

BHAVINI / PFBR

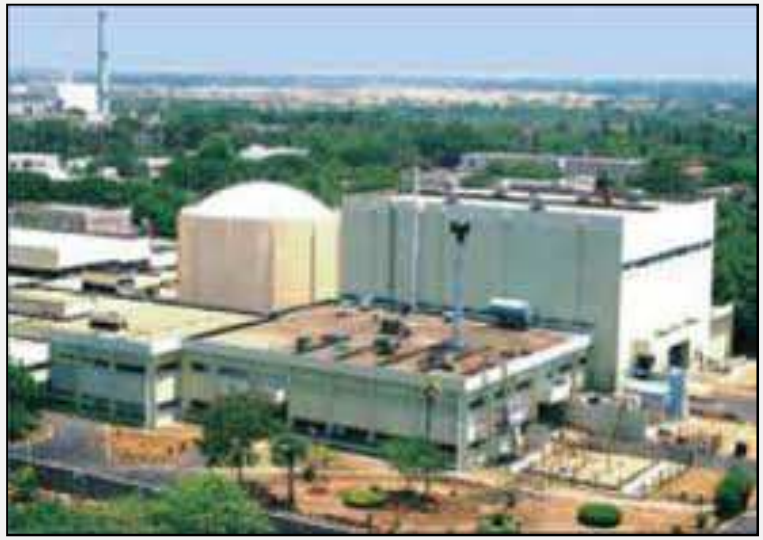
PRP

Study area showing the station location





COASTLINE OF KALPAKKAM



CLIMATOLOGY OF THIS AREA

(i) North-east monsoon (NE monsoon: October – January)

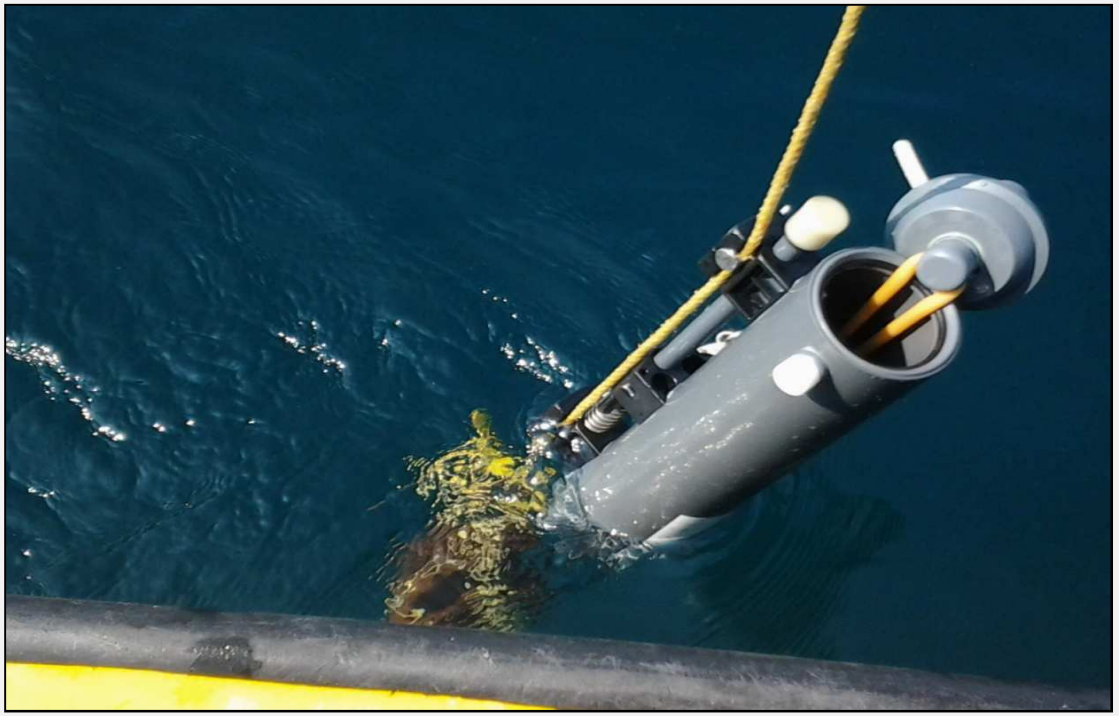
(ii) Summer (Summer: Feb – May)

(iii) South-west monsoon (SW monsoon: June – Sept)

Sampling Methodology

- **Monthly samples were collected for a period of two years (September 2012 – August 2014)**

Sampling Methodology



Digestion Procedure

Water	Zooplankton	Fish	Sediment
50ml	0.2gm	0.2gm	1gm
↓	↓	↓	↓
Chelex-100 resin, 1M CH_3COOH & 2N HNO_3	HNO_3: $HClO_4$	HNO_3: Ultra Pure water	$HClO_4$: HF
↓	↓	↓	↓
shaking 3hr in mechanical shaker then centrifuged at 5000 rpm for 15 min	open digestion: 165°C, 5hr	microwave digestion: 675W, 5 min	residue was dissolved in concentrated HCl and diluted to 25 ml
↓	↓	↓	↓
Analyzed by ICP-MS	Analyzed by ICP-MS & ICP-OES	Analyzed by ICP-MS	Analyzed by ICP-AES

Results

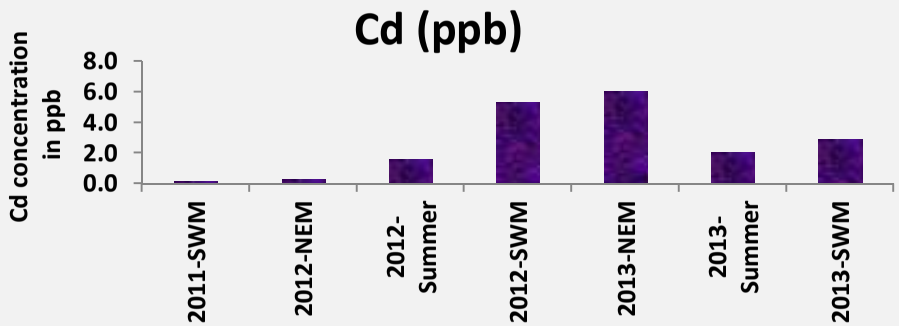
Physicochemical & Meterological Parameters:

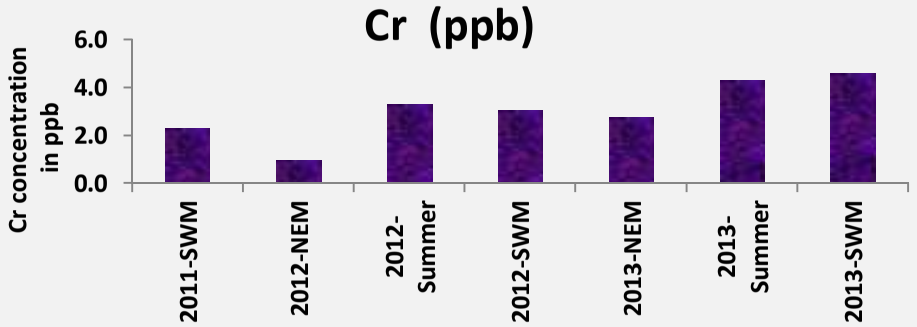
Parameters	Range	Mean
Seawater Temperature (°C)	23 – 31.5	
Atmospheric Temperature (°C)	21 – 35.0	
Rainfall (mm)	568.1 – 2144.3	1298.96
Salinity (PSU)	23.38 – 35.97	32.79
Dissolve Oxygen (mg L^{-1})	3.3 – 6.6	5.49
NO_2 (µmol. L^{-1})	BDL – 5.23	0.58
NO_3 (µmol. L^{-1})	BDL – 69.18	11.49
NH_3 (µmol. L^{-1})	0.03 – 2.95	0.78
TN (µmol. L^{-1})	3.74 – 267.68	33.90
PO_4 (µmol. L^{-1})	BDL – 4.29	0.39
TP (µmol. L^{-1})	0.14 – 4.44	0.63
SiO_4 (µmol. L^{-1})	5.19 – 38.43	10.68
Chlorophyll a (µg L^{-1})	2.5 – 5.6	2.0

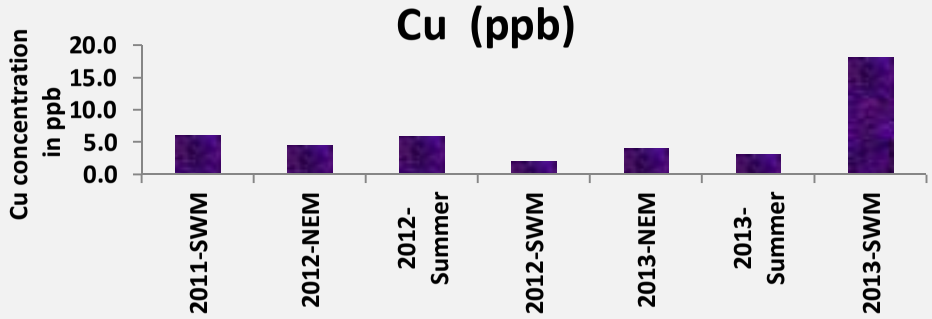
Heavy metal concentration in seawater CRMs: “CASS-5 & NASS-6”

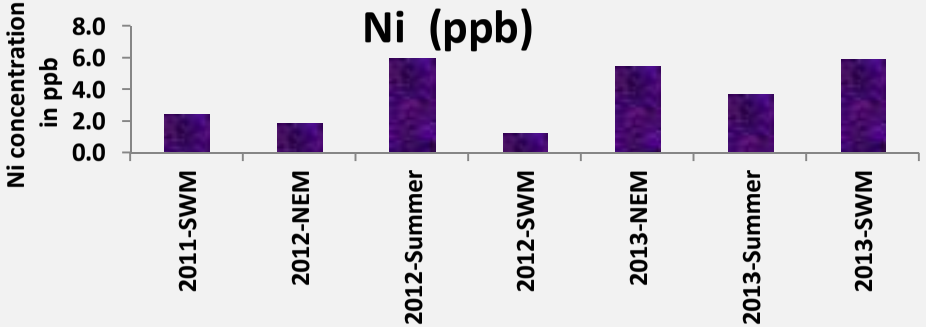
	Certified values (µg/l)		Measured values (µg/l)		Recovery
Metal	CASS-5	NASS-6	CASS-5	NASS-6	(%)
Cr	0.106 ± 0.103	0.118 ± 0.008	0.086 ± 0.010	0.089 ± 0.009	78.4 ± 3.2
Mn	2.62 ± 0.20	0.530 ± 0.050	2.416 ± 0.217	0.452 ± 0.036	88.7 ± 3.5
Co	0.095	0.015	0.078 ± 0.005	0.011 ± 0.001	78.2 ± 3.6
Ni	0.330 ± 0.023	0.301 ± 0.025	0.283 ± 0.025	0.229 ± 0.025	80.9 ± 4.8
Cu	0.380 ± 0.028	0.248 ± 0.025	0.325 ±0.023	0.206 ± 0.016	84.3 ± 1.2
Zn	0.719 ± 0.068	0.257 ± 0.020	0.0771 ± 0.092	0.262 ± 0.029	104.5 ± 2.7
Cd	0.0215 ± 0.0018	0.0311 ± 0.0019	0.018 ± 0.002	0.024 ± 0.002	79.1 ± 2.7
Pb	0.011 ± 0.002	0.006 ±0.002	0.010 ±0.001	0.005 ± 0.001	85.8 ± 4.6

Seasonal variation in trace metal concentration in sea water in Kalpakkam Coast.





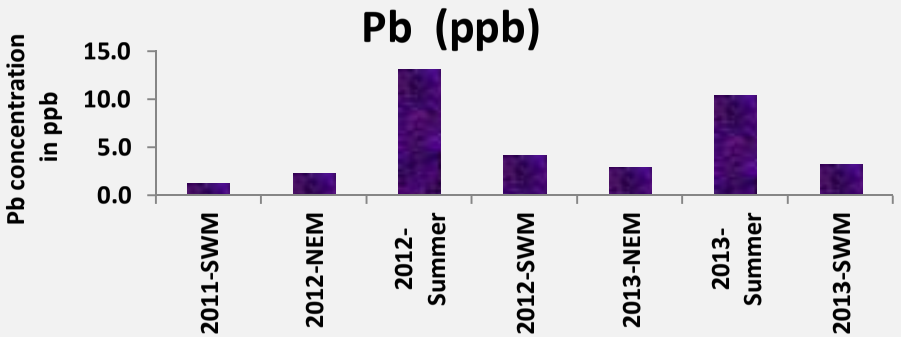


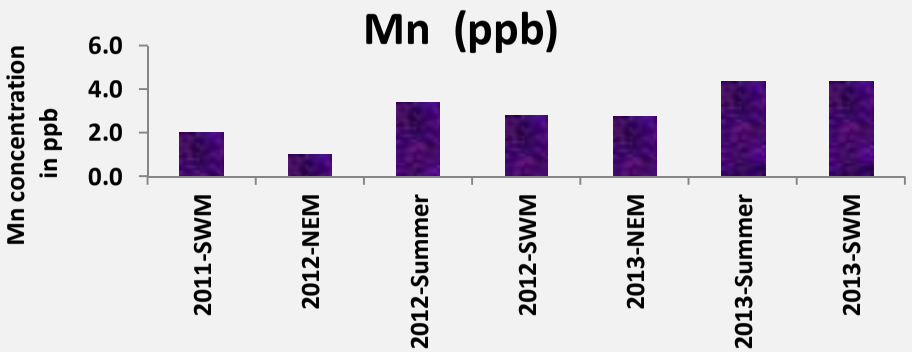


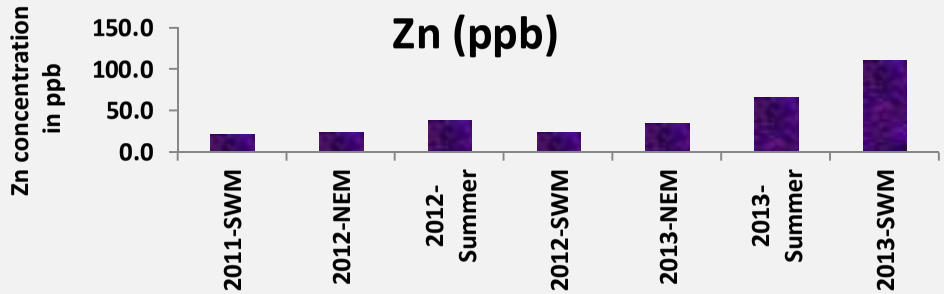
Metals	Range (ppb)	Permissible Limit (ppb)
Cd	1.00 – 17.00	10
Cr	0.50 – 5.30	100
Cu	0.60 – 25.00	20
Ni	0.40 – 14.00	10

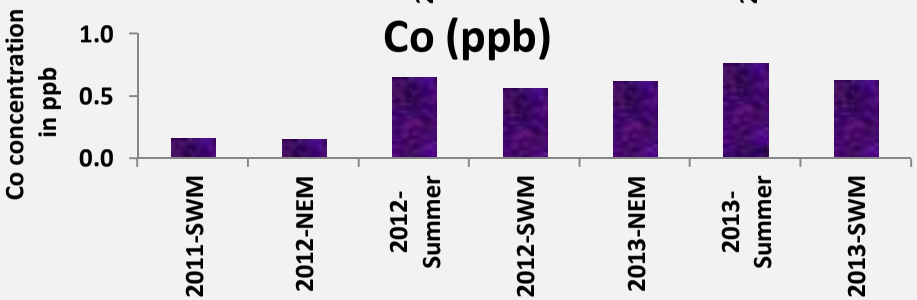
SWM: Southwest Monsoon
NEM: Northeast Monsoon

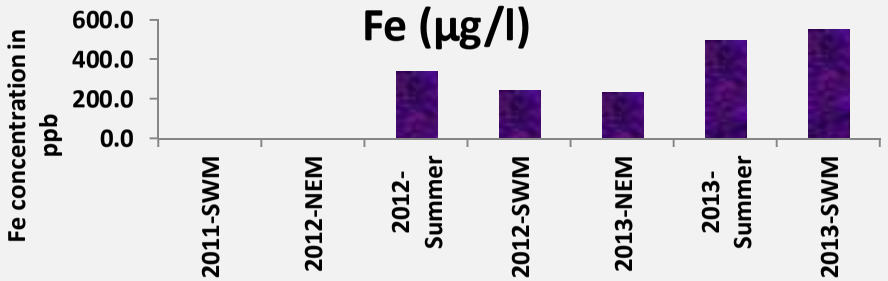
Seasonal variation in trace metal concentration in sea water in Kalpakkam Coast.











SWM: Southwest Monsoon
NEM: Northeast Monsoon

Metals	Range (ppb)	Permissible Limit (ppb)
Pb	1.60 – 35.00	100
Mn	0.80 – 7.00	100
Co	0.49 – 1.31	5
Zn	1.00 – 128.00	100
Fe	58.0 – 979.0	100

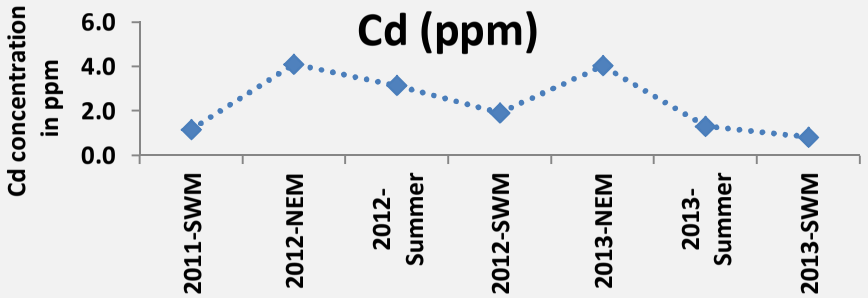
Comparison of trace metal concentrations in seawater (µg/L)

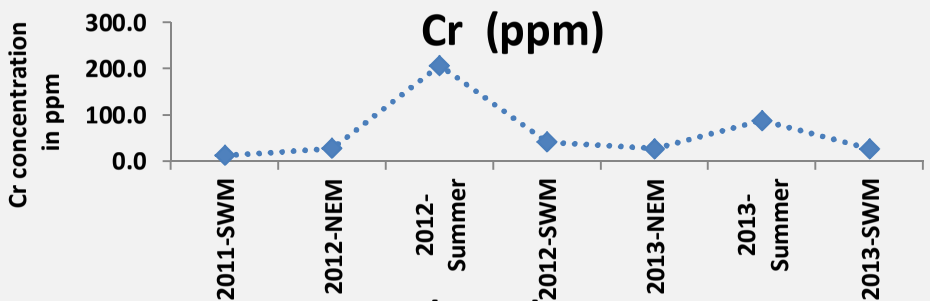
Study area	Cd Mean Range	Cu Mean Range	Pb Mean Range	Zn Mean Range	Ni Mean Range	Cr Mean Range	Mn Mean Range	Fe Mean Range	Co Mean Range	References
Kalpakkam Coast, 2012-2014	3.1	6.7	7.8	53	3.9	3.6	3.5	373.5	0.7	Present study
	1.0-17.0	0.6-25.0	1.6-35.0	1.0-128.0	0.4-14.0	0.5-5.3	0.8-7.0	58.0 – 979.0	0.5-1.3	
Kalpakkam Coast, 2010-2011	0.3	4.06	5.03	35.1	4.3	0.3	3.07		0.1	Padhi et al., 2013
	0.2-0.5	3.5-4.9	1.2-8.1	26.5-44.2	2.8-5.3	0.1-0.5	1.3-4.1		0.04-0.1	
Kalpakkam Coast, 2010	0.06 – 0.1	2.0 – 2.2						26 - 85		Rajamohan et al., 2010
India										
Inshore waters of western Bay of Bengal		5.3		25.4	6.1		3.5			Rajendran et al., 1982
Coastal waters, Visakhapatnam, 1982-1984	0.5-1.2	0.5-2.9	6.5-12	2.9-22	0.8-1.8		2.8-7.7		ND	Satyanarayana et al., 1985
Saurashtra Coast, 1986		5.7-8.00		10.5-11.8	2.6-3.05		8.8-10.4		0.7-0.8	Rao & Indusekhar, 1986
Coastal waters of northern Bay of bengal	1	2.3	6.7	25.3	2		3.5			Satyanarayana et al., 1987
Coastal waters, Gulf of Mannar	1.8		8.96	15.2	3.12	2.84	9.21			Jonathan, 1985
Kalpakkam coastal waters, Bay of bengal		440.525								Selvaraj, 1999
Palk Bay & Gulf of Mannar, 2003-2004	25	6.7		119.8						Sulochanan, 2007
Coastal waters of Cuddalore, 2001	0.4	4.8	12.5	14.3	4.32	1.67	22.2		0.8	Jonathan et al., 2008
Pondicherry, 2010	0.2-5.3	1.2-10.7	1.2-47.5	6.1-80.1		0.5-10.5	2.3-51.3			Solai et al., 2010
Coastal waters of Coromandel coast, Bay of Bengal-(1989-1990)										Govindasamy Azariah , 1999
Mahabalipuram	11.3	10.8		33.7	3.8				1	do
Pondicherry	12.3	3.7		45.3	0.8				3	do
Coastal waters of Coromandel coast, Bay of Bengal-(1990-1991)										do
Mahabalipuram	33.9	17.4		57.8	5.4				2.7	do
Pondicherry	29	11.7		78.3	5.4				2.8	do
Madras Coast	1.0-4.0	6.0-170.0		15.0-290.0	5.00-17.00					Daniel A, 1987
Bay of Bengal		5.4		25.4					1.1	Rajendran et al., 1993
Bay of Bengal	0.3-2.9	1.2-17.5		1.9-174.0	0.8-30.3					Quasim S Z & Sen Gupta R, 1983

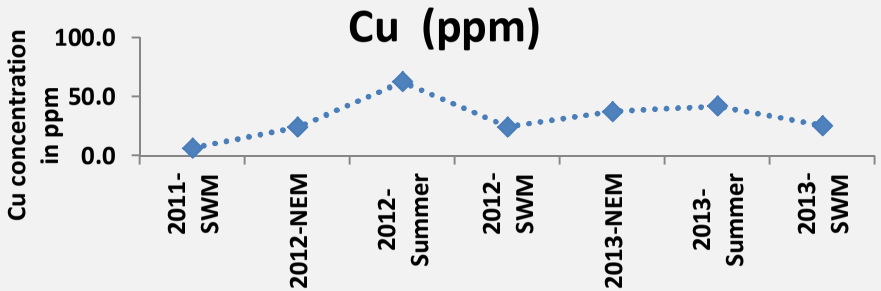
Heavy metal concentration in certified reference material "Mussel Tissue 2977" for Zooplankton:

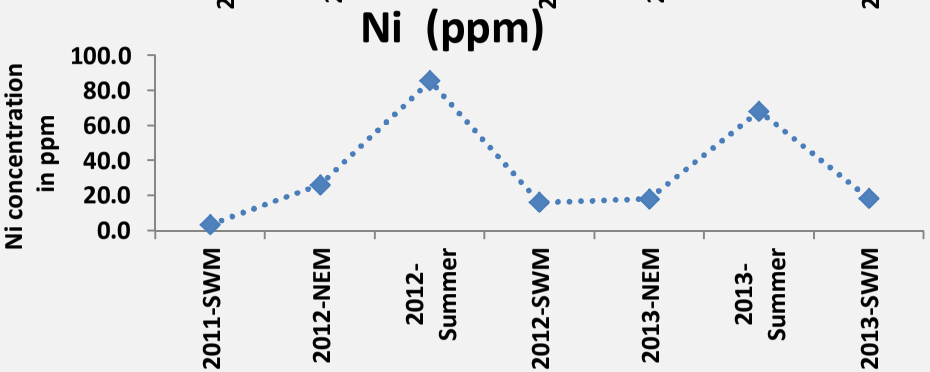
Concentration (PPM)			
Metals	Certified Values	Measured Values by open digestion	Recovery (%)
Cu	9.4	10	106.38
Zn	135	123.3	91
Mn	23.9	23.33	98
Fe	274	260	95
Pb	2.27	BDL	BDL
Cr	3.91	3.33	85

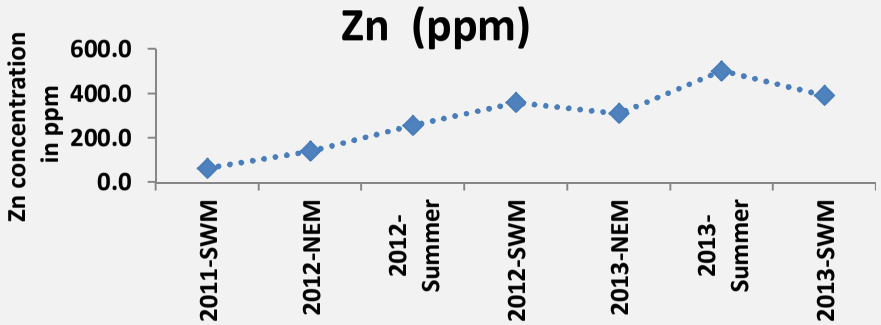
Seasonal variation in trace metal concentration in Zooplankton tissue at Kalpakkam Coast.







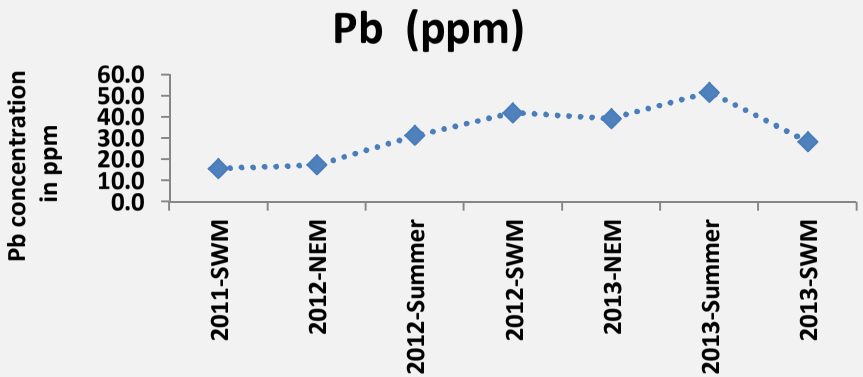


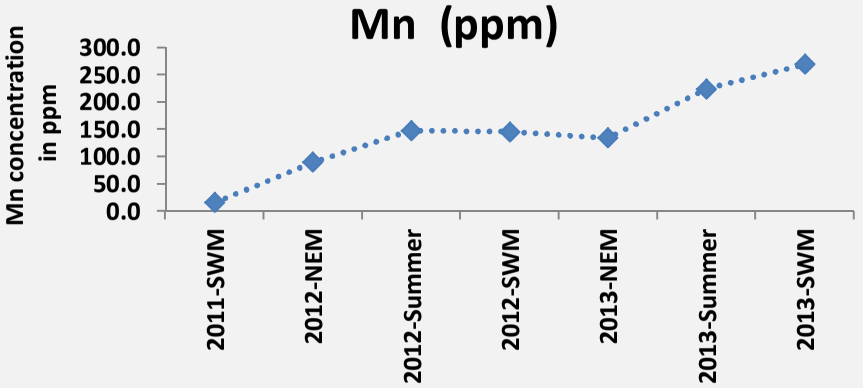


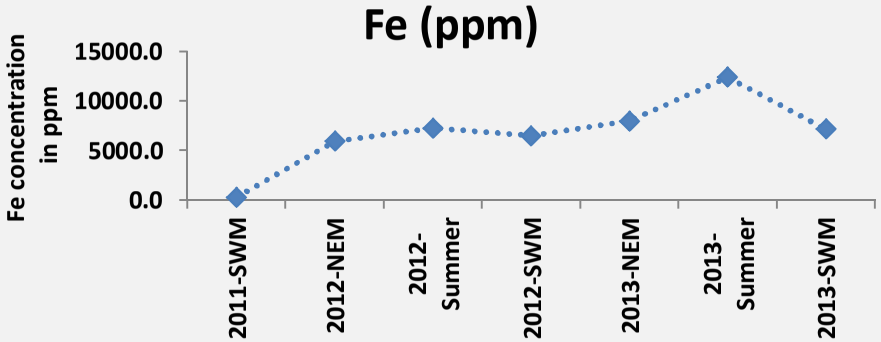
SWM: Southwest Monsoon
NEM: Northeast Monsoon

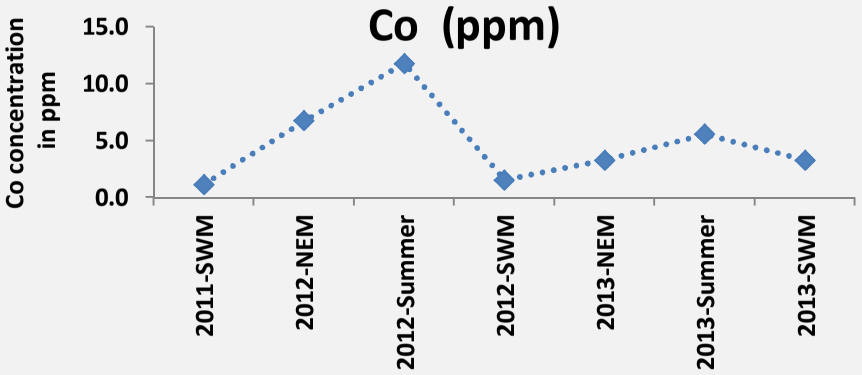
Metals	Range (ppm)
Cd	0.39 – 13.33
Cr	4.65 – 451.30
Cu	5.65 – 105.00
Ni	1.94 – 180.30
Zn	13.04 – 711.75

Seasonal variation in trace metal concentration in Zooplankton tissue at Kalpakkam Coast.









SWM: Southwest Monsoon
NEM: Northeast Monsoon

Metals	Range (ppm)
Pb	4.47 – 84.81
Mn	15.88 – 655.75
Fe	290 - 18060
Co	0.39 – 37.50

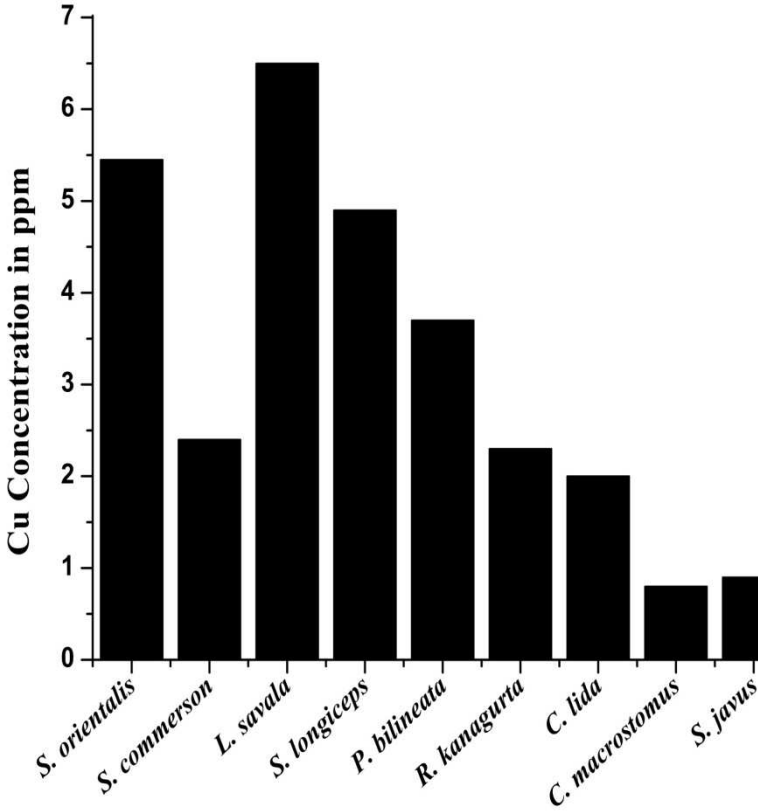
Comparison of trace metal concentrations in Zooplankton tissue (µg/g d.w.)

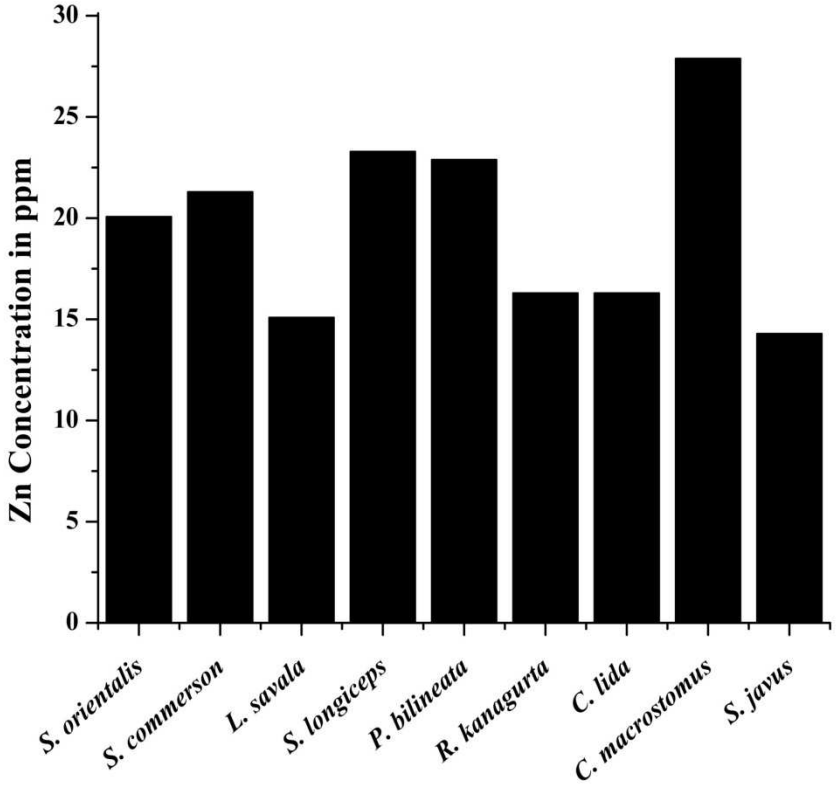
Study area	Cd Mean Range	Cu Mean Range	Pb Mean Range	Zn Mean Range	Fe Mean Range	Ni Mean Range	Cr Mean Range	Co Mean Range	Mn Mean Range	References
Kalpakkam Coast	2.5 0.3-13.3	35.21 5.6-105.0	34.4 4.4-84.8	312.4 13.0-711.7	7591.6 290.0-18060.0	38.1 1.9-180.3	64.5 4.6-451.3	5.3 0.3-37.5	158.04 15.8-655.7	Present Study (2011-2013)
Nagapattinam	11.2	23.3	1.4	179.3	1968.1	15.8		17.2		Rejomon et al., 2008
Chennai	38.1	75.3	16.5	5800.3	25437.1	55.1		38.2		do
Kakinada	8.2	19.2	1.8	1358.8	5625.1	18.1		14.1		do
Visakhapatnam	48.8	89.5	21.1	8162.2	50999.3	62.1		46.8		do
Gopalpur	12.2	42.2	4.9	1480.2	14200.3	38.8		18.1		do
Paradwip	12.2	45.1	2.1	1205.6	3125.1	21.1		26.1		do
North Sea	1.7	15.2								Zauke et al., 1996
German Bight	2.5	9.7								Zauke et al., 1996
Hong Kong (China)	7.3	14.9								Phillips and Rainbow, 1988
Horkkajarvi, 1997, Finland	0.5	11	2.6	297			2.9			Tinna Tulonen et al., 2006
Horkkajarvi, 1998, Finland	0.3	ND	2.6	145			1.5			do
Majajarvi, 1997, Finland	0.5	307	5.2	230			4.9			do
Majajarvi, 1998, Finland	0.7	ND	9	207			11.2			do
Iso-valkjarvi,1997, Finland	0.4	523	4.7	ND			18.2			do
Pitkaniemenjarvi,1998, Finland	0.9	ND	13.8	191			8.5			do
Gdansk Bay	1.5	25.9	12	550	9000	25	44	1	705	Pempkowiak et al., 2000
Gdansk Deep	1.5	25.9	12	550	9000	25	44	1	705	do
Southern baltic	1.6	10	1	159	330	5.5	6	0.6	80	do
Pomeranian Bay	1.6	10	1	159	330	5.5	6	0.6	80	do
Bahamas		90		800	3400	57		3	34	Szabo, 1968

Heavy metal concentration in certified reference material “Mussel Tissue-2977” for Fish

Element	Certified value PPM	Measured value PPM	Recovery %
Cr	9.4	9	95.7
Zn	135	103	76.3
Mn	23.9	20	83.7
Fe	274	292	106.6
Pb	2.27	2.2	96.9
Cr	3.91	3.3	84.4

Heavy metal concentrations (in ppm) in muscle tissue of fishes from Kalpakkam coast. Columns left blank are values below detection limit (<0.02 ppm). Permissible limit (WHO 1989)

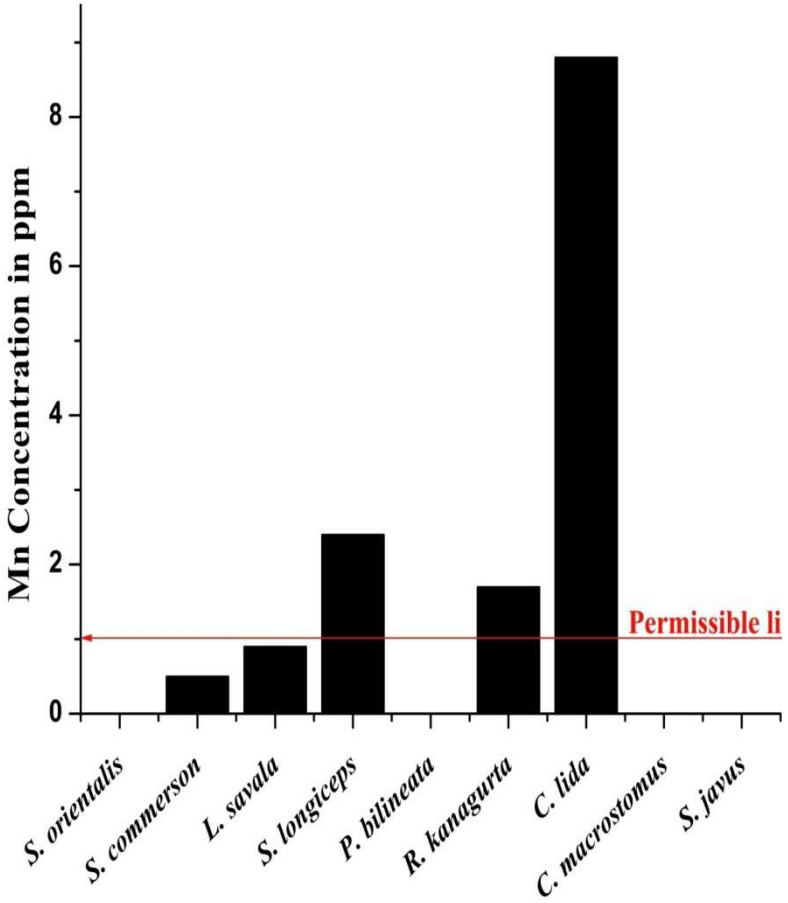


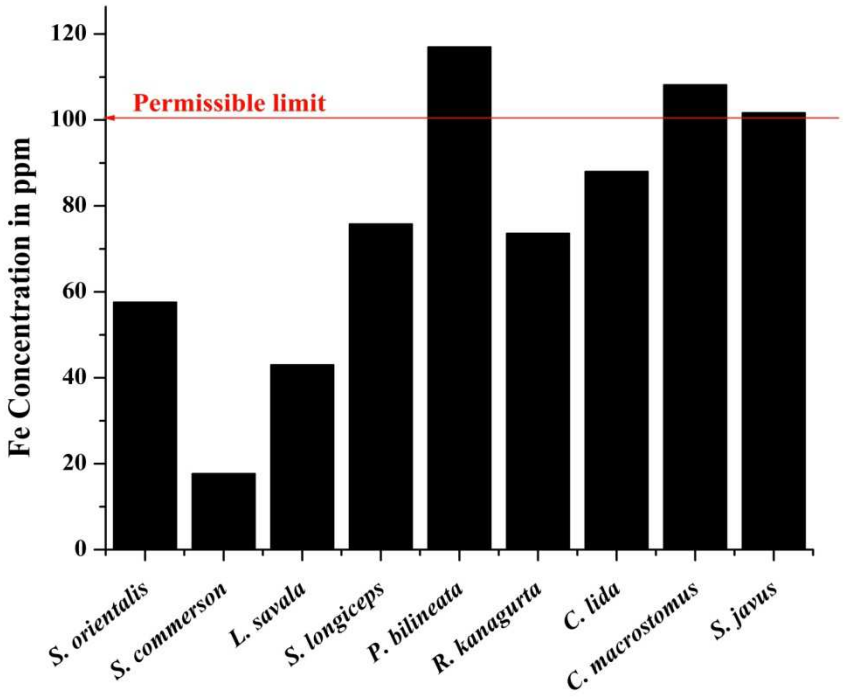


	Cu	Zn	Mn	Fe	Pb	Cr	Reference
WHO	30	100	1	100	2	50	WHO, 1989
FAO	10-100	30-100	-	-	0.5-6.0	1	Naven, 1983

Permissible limit of trace metals for Fish Tissue

Heavy metal concentrations (in ppm) in muscle tissue of fishes from Kalpakkam coast. Columns left blank are values below detection limit (<0.02 ppm). Permissible limit (WHO 19890





***Columns left blank are values below detection limit (<0.02 ppm) Permissible limit (WHO, 1989)**

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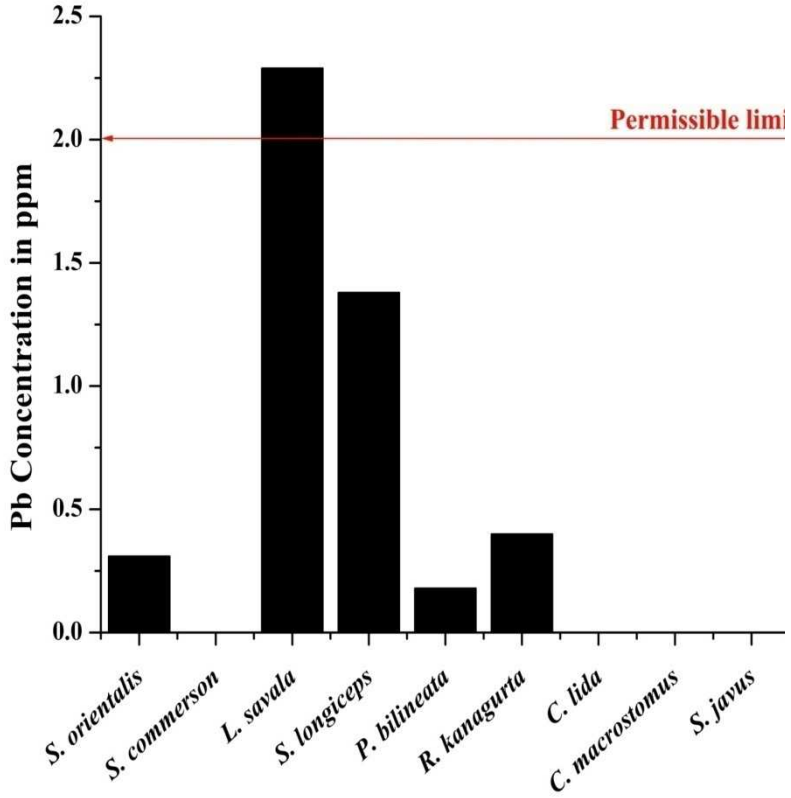
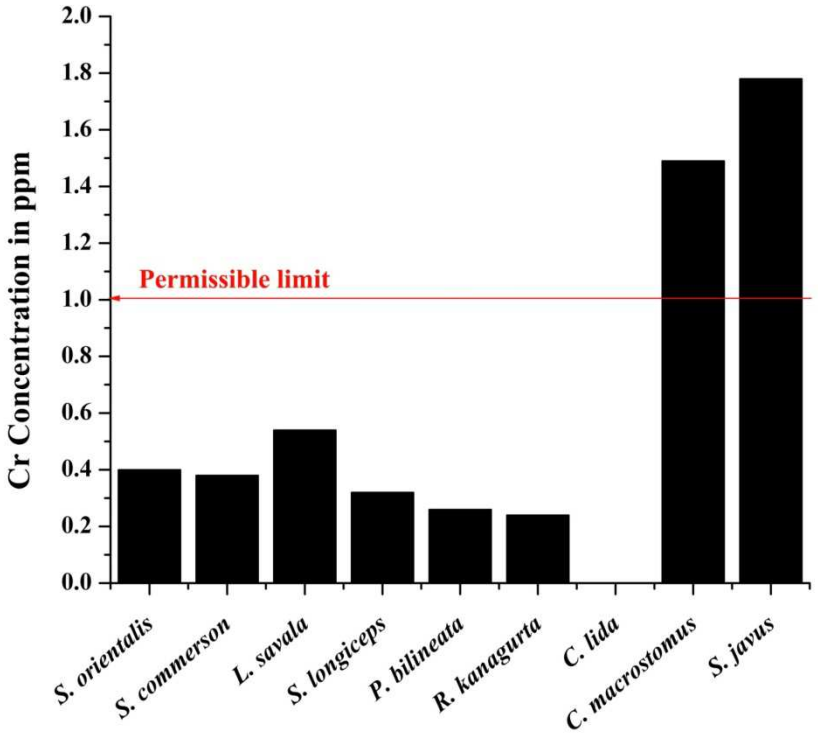


*Columns left blank are values below detection limit (<0.02 ppm)
Permissible limit (WHO, 1989)



*Columns left blank are values below detection limit (<0.02 ppm)
Permissible limit (WHO, 1989)

Bioaccumulation factor in Zooplankton and Fish

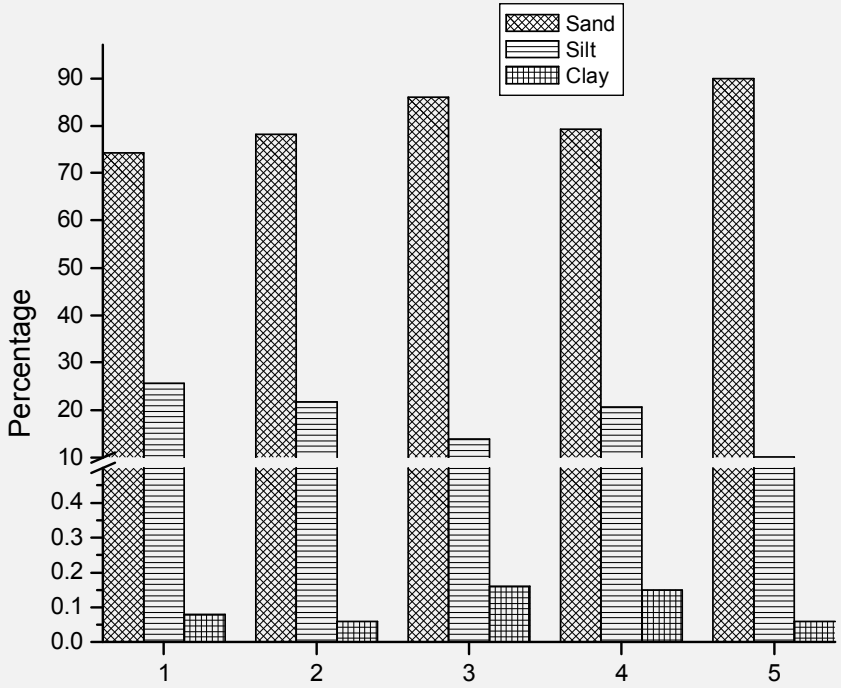
	Cd	Cu	Pb	Cr	Mn	Co	Ni	Zn	Fe
Seawater (ppm)	0.003	0.006	0.006	0.003	0.003		0.004	0.046	0.367
Zooplankton (ppm)	2.527	35.213	34.465	64.566	158.0	5.35	38.1	312.47	7591.6
Fish (ppm)		3.22	0.51	0.60	1.59			19.72	75.84
(BAF) for Zooplankton (ppm)	842	5868	5744	21522	52678		9525	6792	20685
(BAF) for Fish (ppm)		536	85	200	530			428	206

*Average concentration of trace metals (Two year period) and average bioaccumulation factor (BAF) for trace metals in zooplankton and Fish from the coastal waters of Kalpakkam, Southeast Coast of India.

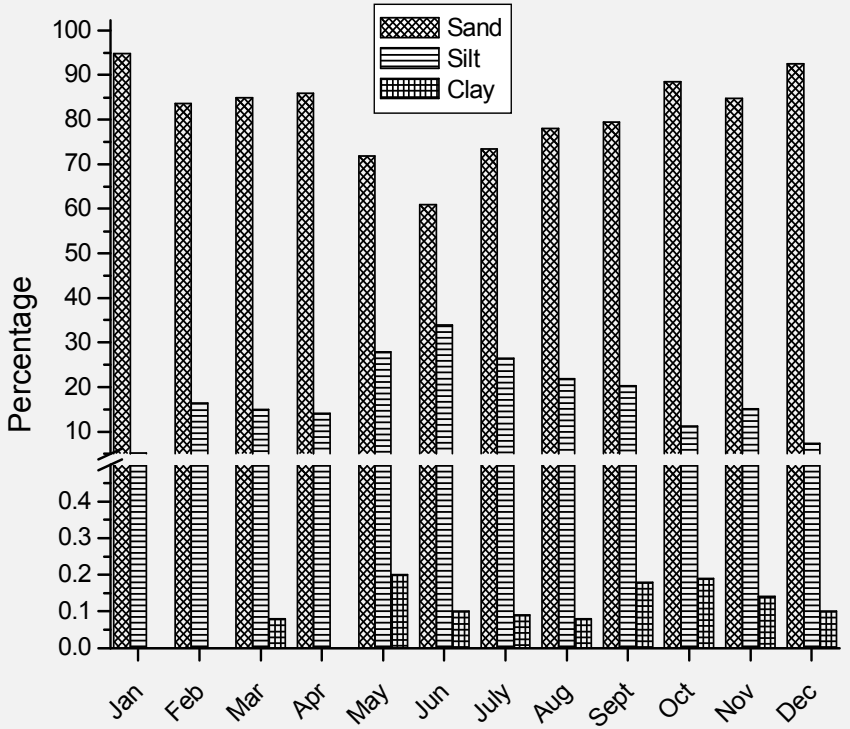
Heavy metal concentration in certified reference material “MAG-1” for Sediment

Element	Certified value PPM	Measured value PPM	Recovery %
Cr	97.00±8.00	97.09	100.09
Ni	53.00±8.00	53.23	100.43
Cu	30.00±3.00	30.69	102.30
Zn	130.00±6.00	129.14	99.34
Pb	24.00±3.00	24.15	100.63

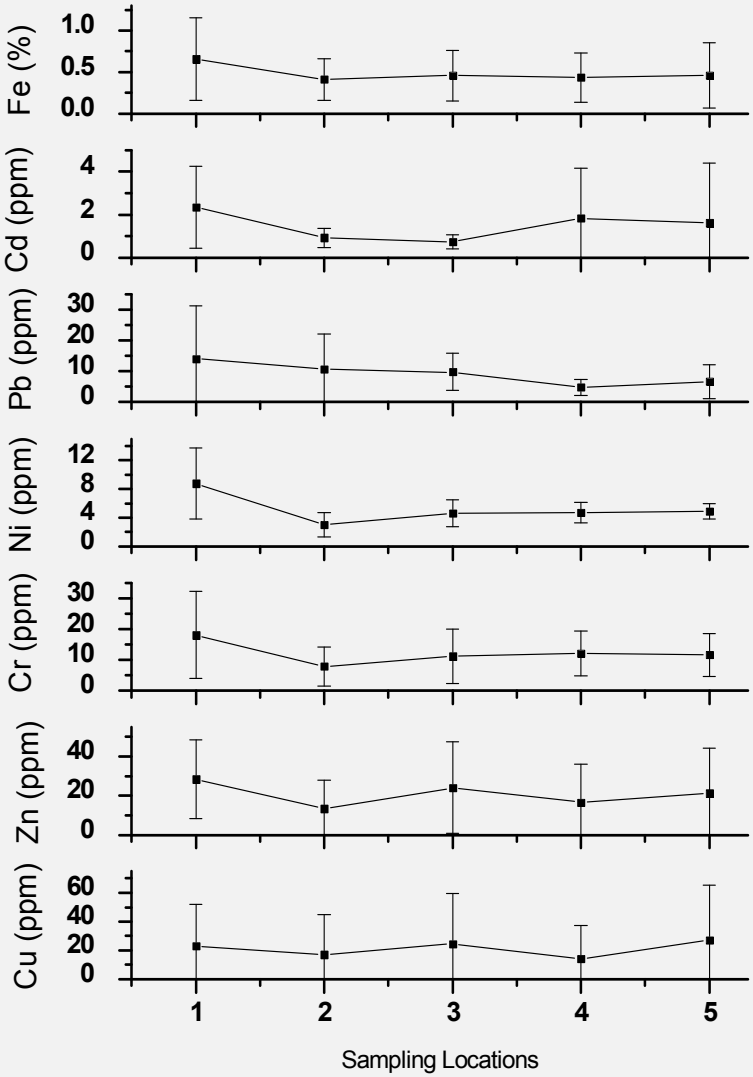
Spatial variations in sand, silt and clay percentage (annual average of each parameter for respective locations) in the coastal sediment at Kalpakkam



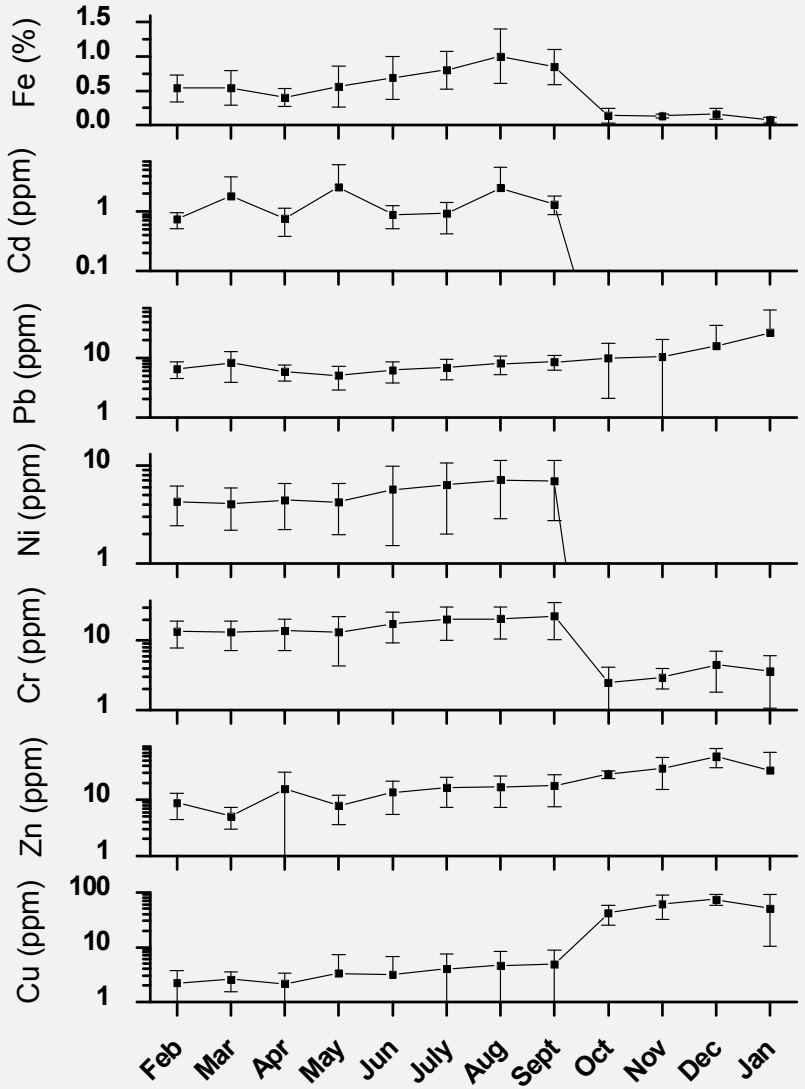
Monthly variations in sand, silt and clay percentage in the coastal sediment at kalpakkam



Spatial variations in heavy metal concentrations (annual average of metal concentrations for respective locations) in the coastal sediment at Kalpakkam



Monthly variations in heavy metal concentrations in the coastal sediment at Kalpakkam



Geoaccumulation Index (I_{geo})

	Cu	Zn	Cr	Ni	Pb	Cd
Monthly						
Feb	-4.08	-3.15	-1.95	-2.74	-1.77	2.30
Mar	-3.88	-3.93	-1.98	-2.81	-1.42	3.62
Apr	-4.14	-2.31	-1.92	-2.70	-1.93	2.34
May	-3.52	-3.31	-1.99	-2.75	-2.15	4.13
Jun	-3.58	-2.52	-1.57	-2.32	-1.84	2.55
July	-3.23	-2.24	-1.37	-2.18	-1.69	2.62
Aug	-3.01	-2.20	-1.35	-2.01	-1.47	4.05
Sept	-2.97	-2.12	-1.21	-2.03	-1.37	3.16
Oct	0.16	-1.45	-4.41	0	-1.17	0
Nov	0.69	-1.10	-4.15	0	-1.10	0
Dec	0.99	-0.39	-3.56	0	-0.50	0
Jan	0.44	-1.21	-3.87	0	0.27	0
Station-wise						
1	-0.71	-1.46	-1.53	-1.70	-0.66	3.97
2	-1.13	-2.54	-2.73	-3.22	-1.06	2.62
3	-0.61	-1.70	-2.24	-2.62	-1.20	2.31
4	-1.40	-2.23	-2.11	-2.59	-2.24	3.61
5	-0.48	-1.88	-2.17	-2.53	-1.75	3.43

Mean concentrations of metals in surface sediments Kalpakkam coast, the Bay of Bengal, compared with that of other coastal regions of the world and crustal average & the upper crust

	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Al (%)	Fe (%)
Present study Range (Mean±SD)	1.1-42.1 (12.2±9.5)	0.9-112.2 (21.3±30.7)	1.0-14.3 (5.2±3.1)	0.1-69.2 (9.1±10.2)	0.7-91.7 (20.8±20.5)	0.1-9.0 (1.5±1.9)	0.28-34.09 (5.37±7.13)	0.02-1.48. (0.48±0.36)
1. Kalpakkam coast	24-111	7-44	22-44	9-28	44-163	0.12-0.31	0.73-4.13	0.18-2.69
2. Shallow cores sediment, the	84	26	64	--	--	--	7.6	3.9
3. Bed sediments, River Palar	338	64	--	45	--	--	--	--
4. Intertidal sediments, SE Coast of India	11–394	0–105	--	5–130	13–144	--	--	2.89
5. Core sediments, Adyar Estuary, SE Coast of India	318	--	426	2	168	--	--	--
2. 0–1 cm interval, Mamallapuram	87	–	53	13	106	–	--	--
3. 0–1 cm interval, Marakkanam	58	–	12	11	87	–	--	--
6. Surface sediments, the Gulf of Mannar	167	–	24	16	73	0.20	--	--
Core sediments, Ennore Creek, SE Coast of India	643	–	49	17	105	0.108	6.42	4.24
7. Bombay coast	103	100.9	52	16.4	96.2	--	--	6.8
8. Gulf of Mannar, Tuticorin coast	177	57	24	16	73	0.16	5.39	1.26
9. Ennore, Bay of Bengal	194.8	506.2	38.6	32.3	126.8	6.58	--	2.72
10. Gulf of Aqaba (Red Sea)	15-186	7-27	19-76	83-225	31-260	2-18	--	0.4-2.84
11. Southern california	74-1480	14-937	16-134	19-578	54-2880	1.1-6.6	--	--
12. Halifax Bay	--	7	12	17	33	--	--	1.92
13. China Shelf Sea	61	15	24	20	65	.065	--	3.1
14. Tokyo Bay	77.3	53.47	32.63	50.68	322	0.996	--	3.77
15. Narragansett Bay	155	190	28	140	250	--	--	3.3
16. Boston Harbour	231.5	112	34.7	135	176	--	--	3.75
17. Gulf of St. Lawerence	87	25	36	21	84	--	--	--
18. Crustal average	100	55	75	12.5	70	0.20	--	--
19. Upper crust	35	25	20	20	71	–	15.2	5
20. Average continental crust	35	25	19	14.8	52	0.1	--	--

1. Selvaraj et al. (2004); 2. Sarin et al. (1979); 3. Mohanachandran (1988); 4. Subramanian and Mohanachandran (1990); 5. Hema Achyuthan et al. (2002); 6. Jonathan and Ram Mohan (2003); 7. Dilli (1986); 8. Jonathan et al. (2004); 9. Muthu Raj and Jayaprakash (2008); 10. Abu-Hilal (1987); 11. Hershelmen et al. (1981); 12. Knauer (1977); 13. Yiyang and Ming-cai (1992); 14. Fukushima et al. (1992); 15. Goldberg et al. (1977); 16. Bothner et al. (1998); 17. Loring (1978, 1979); 18. Taylor (1964); 19. Taylor and McLennan (1985); 20. Wedephol (1995)

Conclusion:

1. Benchmark data for future impact assessment
2. Observed metal concentrations of seawater in Kalpakkam coast is lower than the permissible limit
3. Metal concentration in zooplankton tissue in Kalpakkam coast are low as compared to the other Indian coastal waters
4. The observed lower trace metal concentrations, indicates the unpolluted nature of this location
5. Concentration of Mn, Fe, and Pb in a few species of fish, exceeded the WHO guideline values for safe human consumption. The present study indicated that most of the metal concentrations found in the muscles of the nine fish species were below the prescribed limit values for human consumption
6. Concentration of most of the metals in sediment were found to be lower than the values reported during the pre-tsunami period which could be due to the removal of clayey sediment associated with relatively high concentration of metals from the tsunami
7. The elevated CF and I_{geo} values for Cu and Cd indicated that surface sediment is moderately polluted with Cu and Cd, whereas, all the other metal levels were well within the unpolluted limit


Thank You