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# HEAVY METALS IN WATER, SEDIMENT AND IN SOME SELECTED FISH SPECIES OF THE ENNORE AND CHENNAI FISHERIES HARBOUR, CHENNAI, TAMIL NADU

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## ABSTRACT

Mercury and arsenic are the toxic heavy metals found in water, sediment and in different species of fish tissue, Rastrelliger kanagurta(Indian Mackerel), Nemipterus spp., (threadfin beam), Parapenaeopsis Maxillipedo (shrimp), Metapenaeus dobsoni (shrimp), Perna sp. (bivalve), Sepia sp.(Cephalopod-cuttlefish) and Loligo sp.(Cephalopod-squid) of the Chennai, Ennore estuary. The water, sediment and fish tissues were analysed for mercury and arsenic using standard procedure in Atomic Absorption Spectrophotometry. The maximum mercury concentration in water is 0.02ppb±0.01, in sediment is 0.30 ppb±0.01 and in different fish tissue species in Rastrelliger Kanagurta, 0.25ppb±0.06, Nemipterus spp., 0.54ppb±0.06, Parapenaeopsis Maxilli - pedo 0.58ppb±0.06, Metapenaeus dobsoni, 0.34 ppb±0.06, Perna sp., 0.61ppb±0.06 and Sepia sp. 0.72ppb±0.06 and Loligo sp., Cephalopod-squid, 0.38 ppb±0.06 in the first quarter. Among the fish species selected for the study during Apr-June'09, the lowest mercury content is in Rastrelliger kanagurta (Indian Mackerel), 0.35ppb±0.11 followed by Metapenaeus dobsoni,0.68ppb±0.11, Sepia spp., 0.76ppb±0.11, Loligo sp. (Cephalopod squid), 0.78 ppb±0.11 and Nemipterus spp. (threadfin bream), 1.29ppb±0.11 during second quarter. The percentage increase in mercury during first quarter is 64.67% from lowest to highest. The percentage increase in mercury during second quarter is 55.99% from lowest to highest. The percentage increase in mercury content in  $\mu g/g$  (ppb) was 80.27% from lowest to highest. The metal concentration in tissues  $\mu g/g$  (ppb) ranged between 0.26-1.29µg/g (ppb) in mercury. Among the fish species selected for study for arsenic during Jan-Mar'09, the lowest arsenic content is in Rastrelliger Kanagurta (Indian Mack erel), 3.85ppb±8.22 followed by Nemipterus spp. (threadfin bream), 6.10ppb±8.22, Loligo sp., 26.09ppb±8.22, Metapenaeopsis Maxillipedo (shrimp), 34.72 ppb±8.22, Parapenaeopsis Maxi - millipedo (shrimp), 43.84ppb±8.22, Sepia spp., 52.09ppb±8.22 and Perna sp. (bivalve) 60.13 ppb±8.22 in the first quarter. Among the fish species selected for the study during Apr-June'09, the lowest arsenic content is in Rastrelliger kanagurta (Indrai Mackerel), 4.35ppb±7.88 followed by Nemipterus spp. (threadfin bream), 13.12ppb±7.88, Metapenaeus dobsoni (shrimp) 14.92 ppb± 7.88, Sepia sp., (Cephalopod cuttlefish), 18.74ppb±7.88 and Loligo sp. (Cephalopod -squid) 45.09 ppb±7.88 in the second quarter. The percentage increase in arsenic during first quarter is 93.58%. The percentage increase in arsenic during second quarter is 90.34%. The percentage increase in arsenic content value in µg/g(ppb) was 93.58%. The metal concentration in tissues, µg/g (ppb) ranged between 3.85-60.13µg/g(ppb). The lowest mercury in tissue was found in the species Rastrelliger Kanagurta was 0.25µg/g (ppb)±0.06 and in arsenic it was  $3.85\mu g/g$ , (ppb)  $\pm 8.22$  the highest mercury in tissue was found in the Nemipterus sp., 1.29µg/g(ppb)±0.11, the highest arsenic was found in 60.13µg/g (ppb)±7.88 in Perna sp.(bivalve).

KEY WORDS : Arsenic, Mercury, Water, Sediment, Fish, Estuary

## INTRODUCTION

Heavy metals viz. arsenic and mercury are known toxic elements present in fishes, its surrounding water and sediments. These heavy metals if present in trace amounts are negligible and if present in higher amounts are hazardous to human health. These heavy metals are found in sea water due to effluents discharged from the industries/factories surrounding Ennore. The important heavy metals found in these area are mercury and arsenic. The presence of mercury can affect the brain development of older children. These heavy metals may be present in water, sediment and fish tissues of the Ennore region. In the present study, the presence of heavy metals viz. mercury and arsenic in particular in water, sediment and in some selected fish species of the Ennore and Chennai were studied. The present work was carried out at the Ennore, Chennai. Ennore is a known industrial area and the pollutants from industries are discharged into the sea. The pollutants are known to have heavy metals, viz. arsenic and mercury.

#### MATERIALS AND METHODS

**Samples collection:** The water samples collected (100ml) at quarterly intervals during the period Jan-Dec, 2009 from both Ennore and Chennai Fisheries harbour in labelled bottles were taken for analysis. The sediment samples, (100g) were collected and dried in a hot air oven at 60 °C and then powdered and packed in properly labeled polythene covers and stored in the refrigerator and then taken for analysis of heavy metals.

#### **Mineral Analysis**

Live specimens of the different species of fish samples, Rastrelliger kanagurta,(1) Nemipterus spp., (2), Parapenaeopsis maxillipedo,(3) Metapenaeus dobsoni, (4), Perna sp. (bivalve), (5) Sepia sp.(Cephalopod-cuttlefish)(6) and Loligo sp. (Cephalopod-squid)(7) were collected at random from Marina(Nochikuppam), Chennai. The study was conducted for 12 months from Jan to Dec'2009. The weight of the sample taken for analysis was 10g. The samples were stored at 0°C in the refrigerator for further analysis. Heavy metals analysed were mercury and arsenic. Total mercury content in water, sediment and biological samples were estimated using Atomic absorption spectrophotometry. Data obtained were subjected to

analysis of variance at 95% confidence limit. 10 samples of each species were purchased monthly from Marina for the study. The soft tissues of each species were extracted, weighed and dried in the laboratory oven for three days in hot air oven at a constant temperature of 60 °C. The dried samples were weighed and homogenized in a porcelain mortar and stored in an airtight container. Weigh (0.5-1g) material (dry weight) of 1-5g (wet wt). Add 3 drops of sodium chloride and 8 ml of acid solution, heat at 70 °C for 12h in water bath or other heating equipment. Add 3 drops of hydroxyl ammonium chloride solution. Mix and dilute to 50 ml with metal free distilled water, (filter through N-42 filter paper) and take readings using Atomic absorption spectrophotometer. The digestion procedure followed was similar to that of water and sediment. (Kaladharan et al., 2001).

The lower limit of detection for mercury using this method was 0.001ppm. The statistical analysis were done using SPSS 16.0 and graphs were drawn using Minitab (Version 15.0)

#### **RESULTS AND DISCUSSION**

Heavy metal contamination in marine environments has emerged as a critical factor on emerging global environmental issue as it poses a threat to marine life (Qian et al., 2015). The metal pollution could also affect the socio-economic structure of the region as seafood in terms of domestic consumption and international trade (Freije, 2015; Hussain et al., 2020). Mercury: The different species taken for study include Rastrelliger Kanagurta, (Indian Mackerel), Nemipterus spp. (threadfin bream), Parapenaeopsis mexillipedo (shrimp), Metapeneaeus dobsoni (shrimp), Perna spp. (bivalve), Sepia sp. (Cephalopod cuttlefish) and Loligo sp. (Cephalopod-squid). Sediment analysis, 2009, mercury level ranged between 0.14-0.30 ppb±0.07 in Chennai fisheries harbour, in Ennore location the mercury was 0.52-6.16ppb±0.02. In Ennore location the mercury content is higher than in Chennai fisheries harbour region due to effluent discharge in the industrial area. Coastal sediments are always the final repository of contaminants originating from the multiple sources and usually act as important sinks for trace elements through adsorption and subsequent sedimentation (Chapman et al., 1998; Zwolsman et al., 1997). The water sample heavy metal analysis in Ennore region varies from 0-0.02ppb±0.01 in mercury. In Chennai Fisheries harbour region the water sample heavy

metals, mercury ranges from 0-0.02ppb±0.01. The water sample pollution level is same in Ennore and Chennai Fisheries region of Chennai, TamilNadu. Metals in the coastal waters and sediments harm the ecosystem and the biota due to their bioaccumulation potency that addresses concerns on human health (Sharifuzzaman et al., 2016). The concentrations of heavy metals in fish have been extensively studied in different parts of the world (Elnabris et al., 2013). Most of these studies concentrated mainly on the heavy metals in the fish muscles. Decline in ecosystem productivity, loss of biological diversity, alteration of habitats and contamination of aquatic biota are among the most important effects of these pollutants (Zeitoun et al., 2014). Among the fish species selected for the study during Jan-Mar'09 the lowest mercury content is in Rastrelliger kanagurta (Indian Mackerel), 0.25ppb ±0.06 followed by Metapenaeus dobsoni, 0.34ppb±0.06, Loligo species, 0.38 ppb±0.06, Nemipterus spp., 0.54ppb±0.06, Parapenaeopsis maxillipedo, 0.58ppb±

Table 1a. Heavy metal analysis - water & sediment

0.06, Perna spp., 0.61ppb ±0.06 and Sepia sp., 0.72ppb±0.06. Among the fish species selected for study during Apr-June'09, the lowest mercury content is in Rastrelliger kanagurta (Indian Mackerel), 0.35 ppb±0.11 follow ed by Metapenaeus dobsoni, 0.68ppb±0.11, Sepia spp., 0.76 ppb ±0.11, Loligo sp. (Cephalopod squid) 0.78 ppb±0.11 and Nemipterus spp. (threadfin bream), 1.29ppb± 0.11 during second quarter. The percentage increase from Nemipterus spp. (threadfin bream) to Rastrelliger kana gurta (Indian Mackerel) species is 26.08%, Parapenaeopsis mexillipedo (shrimp) to Nemipterus spp. (threadfin bream) species is 9.92%, Nemipterus spp. (threadfin bream) to Parapenaeopsis mexillipedo (shrimp) species is 29.07%, Perna spp. (bivalve) to Metapeneaeus dobsoni (shrimp) species is 7.53%, Sepia sp. (Cephalopod cuttlefish) to Perna spp. (bivalve) species is 4.80% and Loligo sp.(Cephalopod-squid) to Sepia sp. (Cephalopod cuttlefish) species is 15.50% in the first quarter. The percentage increase from Nemipterus spp. (threadfin bream) to Rastrelliger kanagurta (Indian Mackerel)

Location–Chennai fisheries harbor SNo.	2009	Water sample (ppb) Arsenic-I quarter	Water sample (ppb) Mercury-I quarter	Sediment sample (ppb) Arsenic-II quarter	Sediment sample (ppb) Mercury-II quarter
1	Jan-Mar	0.01	0.02	0.00	0.14
2	Apr-June	0.02	0.00	0.52	0.25
3	July-Sep	0.01	0.00	0.00	0.00
4	Oct-Dec	0.00	0.00	6.16	0.30
	average	0.01	0.01	0.17	0.17
	minimum	0.00	0.00	0.00	0.00
	maximum	0.02	0.02	0.62	0.30
	sem	0.00	0.01	0.02	0.07
	sd	0.01	0.01	0.03	0.13
	CV	4.85	0.05	10.39	0.64
	s/ns	ns	ns	ns	ns

<b>Table 10.</b> Theavy metal analysis – water & seumen	Table 1b. Heav	v metal analy	vsis – water	& sedimen
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Sl. No.	Location-Ennore	Arsenic-I quarter	Mercury-I quarter	Arsenic-II quarter	Mercury-II quarter
1	Jan-Mar	0.01	0.00	0.00	0.14
2	Apr-June	0.02	0.00	0.52	0.25
3	July-Sep	0.01	0.00	0.00	0.00
4	Oct-Dec	0.00	0.00	6.16	0.30
	average	0.01	0.00	0.17	0.17
	minimum	0.00	0.00	0.00	0.00
	maximum	0.02	0.00	0.62	0.30
	sem	0.00	0.00	0.02	0.07
	sd	0.01	0.00	0.03	0.13
	CV	81.65	0.00	17.96	77.11
	s/ns	ns	ns	ns	ns

species is 48%, *Metapeneaeus dobsoni (shrimp*) to *Nemipterus spp. (Threadfin bream*) species is 10.32%, *Metapeneaeus dobsoni (shrimp*) to *Parapenaeopsis mexillipedo (shrimp*) to species is 2.17%, *Perna spp. (bivalve*) to *Metapeneaeus dobsoni (shrimp*) species is 30.55% in the second quarter. The percentage increase in mercury during first quarter is 64.67% from lowest to highest. The percentage increase in mercury during second quarter is 55.99% from lowest to highest. The percentage increase in mercury content from lowest to highest value in µg/ g (ppb) was 80.27%. The metal concentration in tissues µg/g (ppb) ranged between 0.25-1.29 in mercury. The percentage increase in mercury from first quarter to second quarter is 11.33%.

#### Arsenic

The water sample heavy metal, arsenic in Ennore region varies from 0-0.02 ppb  $\pm$  0.01 and in Chennai Fisheries Harbour arsenic value ranges from 0-

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0.01ppb±0.01. The arsenic value of the water sample of the Ennore is more than that of the Chennai fisheries region and the pollution from the industrial area is more. In the sediment analysis, arsenic level ranges between 0.14-0.52 ppb±0.02 in Chennai fisheries harbour region and in Ennore it was 0-6.16 ppb±0.07. The sediment indicates the higher amount of heavy metal, arsenic present and this represents the amount of heavy metal in the marine fishes also. Among the fish species selected for study for arsenic during Jan-Mar'09, (I quarter) the lowest arsenic content is in Rastrelliger kanagurta (Indian Mackerel), 3.85 ppb±8.22 followed by Nemipterus spp. (threadfin *bream*), 6.10 ppb±8.22 < Loligo *sp.* 26.09 ppb±8.22 <*Metapenaeopsis mexillipedo (shrimp)*, 34.72 ppb±8.22 < Parapenaeo- psis maxmillipedo (shrimp) < 43.84 ppb ± 8.22 *<Sepia* spp., 52.09 ppb ± 8.22. Among the fish species selected for study during Apr-Jun'09, (II quarter) the lowest arsenic content is in Rastrelliger kanagurta (Indrai Mackerel), 4.35ppb±7.88 followed

SN.	Species	Mercury (ppb)- I quarter	Arsenic (ppb) -I quarter	Mercury (ppb)- II quarter	Arsenic (ppb) -II quarter
1	Rastrelliger Kanagurta	0.25	3.85	0.35	4.35
2	Nemipterus sp.	0.54	6.10	1.29	13.12
3	Parapenaeopsis maxillipedo	0.58	43.84	0.58	43.84
4	Metapenaeus .dobsoni	0.34	34.72	0.68	14.92
5	Perna sp.(bivalve)	0.61	60.13	0.61	60.13
6	Sepia sp. (cephalopod, cuttlefish)	0.72	52.09	0.76	18.74
7	Loligo sp.(cephalopod-squid)	0.38	26.09	0.78	45.09
	average	0.49	32.40	0.72	28.60
	minimum	0.25	3.85	0.35	4.35
	maximum	0.72	60.13	1.29	60.13
	sem	0.06	8.22	0.11	7.88
	sd	0.17	21.75	0.29	20.86
	CV	34.46	67.14	40.03	72.93
	s/ns	S	s	S	S

Table 3. Anova table for first and second qua	rter
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quarter:						
Variation	df	SS	Quot	P-val	F-crit	
Between metals	1	3564.98	15.06	0.002	4.74	sig
Between species	12	2839.99	236.66			
Total	13	6404.97				
nd Quarter						
Variation	df	SS	Quot	P-val	F-crit	
Between metals	1	0.42	0.42	2.37	0.18	ns
Between species	5	0.88	0.17			
Total	6	1.31				
	quarter: Variation Between metals Between species Total nd Quarter Variation Between metals Between species Total	quarter:VariationdfBetween metals1Between species12Total13ad Quarter13VariationdfBetween metals1Between species5Total6	quarter:VariationdfssBetween metals13564.98Between species122839.99Total136404.97nd Quarter136404.97VariationdfssBetween metals10.42Between species50.88Total61.31	quarter:VariationdfssQuotBetween metals13564.9815.06Between species122839.99236.66Total136404.97ad QuarterVariationdfssQuotBetween metals10.420.42Between species50.880.17Total61.310.420.42	quarter:VariationdfssQuotP-valBetween metals13564.9815.060.002Between species122839.99236.660.002Total136404.970.0020.002and QuarterVariationdfssQuotP-valBetween metals10.420.422.37Between species50.880.170.17Total61.310.170.17	quarter:VariationdfssQuotP-valF-critBetween metals13564.9815.060.0024.74Between species122839.99236.6600Total136404.97000and QuarterVariationdfssQuotP-valF-critBetween metals10.420.422.370.18Between species50.880.1700Total61.31000

by Nemipterus spp. (threadfin bream), 13.12 ppb ± 7.88< Metapenaeus dobsoni (shrimp), 14.92 ppb±7.88< Sepia sp., 18.74 ppb±7.88, Parapenaeopsis mexillipedo, 43.84 ppb±7.88, Loligo sp. (Cephalopod-squid), 45.09 ppb±7.88 and Perna spp., 60.13 ppb±7.88. The percentage increase in arsenic content value in µg/ g (ppb) was 93.58%. The percentage increase from first quarter in mercury to first quarter in arsenic is 98.48%. The percentage increase form Nemipterus spp. (threadfin bream) to Rastrelliger kana -gurta (Indian Mackerel) species is 13.36%, Parapenaeopsis mexillipedo (shrimp) to Nemipterus spp. (threadfin bream) species is 15.85%, Metapeneaeus dobsoni (shrimp) to Parapenaeopsis mexillipedo (shrimp) species is 26.26%, Perna spp. (bivalve) to Metapeneaeus dobsoni (shrimp) species is 0.71%, Sepia sp. (Cephalopod *cuttlefish*) to *Perna spp.* (*bivalve*) species is 76.62%, Loligo sp.(Cephalopod-squid) to Sepia sp. (Cephalopod cuttlefish) species is 36.78% during first quarter. The percentage increase from Nemipterus spp. (threadfin bream) to Rastrelliger kanagurta (Indian Mackerel) species is 58.42%, Parapenaeopsis mexillipedo (shrimp) to Nemipterus spp. (threadfin bream) species is 25.66%, Metapeneaeus dobsoni (shrimp) Metapeneaeus dobsoni (shrimp) to Parapenaeopsis mexillipedo (shrimp) species is 12.04%, Perna spp. (bivalve) to Metapeneaeus dobsoni (shrimp) species is 66.82% for the second quarter. The

**Table 4.** Cumulative Mercury and Arsenic content in<br/>consecutive 12 months

SNo.	Months	Mercury, (ppb)	Arsenic, (ppb)	incr./decr. (%)
				(bet. metals)
1	Jan	0.25	3.85	93.38
2	Feb	0.54	6.10	91.14
3	Mar	0.58	43.84	98.66
4	Apr	0.34	34.72	99.00
5	May	0.61	60.13	98.91
6	June	0.72	52.09	98.61
7	July	0.38	26.09	98.53
8	Aug	0.35	4.35	91.80
9	Sep	1.29	13.12	90.14
10	Oct	0.68	14.92	95.40
11	Nov	0.76	18.74	95.91
12	Dec	0.78	45.09	98.26
	average	0.61	26.92	95.81
	minimum	0.25	3.85	90.14
	maximum	1.29	60.13	99.00
	sem	0.08	5.70	0.97
	sd	0.28	19.75	3.37
	CV	46.08	73.37	3.52
	s/ns	s	s	s

lowest mercury in tissue was found in the species *R*. Kanagurta was 0.25µg/g±0.06 and in arsenic it was found to be  $3.85\mu g/g \pm 8.22$ , the highest mercury in tissue was found in the species  $1.29\mu g/g(ppb)\pm 0.11$ , the highest arsenic was found in 60.13µg/ g(ppb)±7.88 in Perna sp. (bivalve). The peak arsenic values occurred in the month of May'09 and the peak mercury values occurred in the month of Sep'09. The lowest mercury and arsenic value occurred in the month of Jan'09. The percentage increase from first quarter in arsenic to second quarter is 57.57% and the percentage increase from second quarter of mercury to second quarter of arsenic is 95.97%. The individual effects of mercury and arsenic in water, sediment and fish tissue at both first and second quarters in non significant at 5% level of significance. The effect between metals, viz. arsenic and mercury are significantly different from each other in values at 5% level of significance in the first quarter. In the second quarter the effect between the metals is non significant at 5% level of significance. The interaction effect between two metals, viz. mercury and arsenic is non significant at 5% level of significance. For clear understanding the distribution of the heavy metals, mercury and arsenic the surface plots and contour plots of different species, at different quarters were drawn both for mercury and arsenic. The mercury levels in the samples of the fishes were found below the tolerable limits than the permissible level, i.e., 1ppm. (WHO, FDA, Consumer, September, 1994). The normal permissible standard values for mercury and arsenic in fish is 1mg/kg and 10-400 mg/kg. The Food and Drug Administration (FDA) has set a maximum permissible level of one part of methyl mercury in a million parts of seafood (1ppm). Some of the metals found in fish might be essential as they play important roles in the biological system of the fish as well as in human beings, some of them may also be toxic as they might severely damage human health even in trace amounts. (Lenin Raj et al., 2010). Certain aquatic organisms are accumulating mercury from the environment through different trophic levels. (Rajathy, 1997). The normal permissible level of arsenic and mercury in water is 0.50-0.20 mg/l (Jacquiline Lam and Glenn Sia Su, 2009). The normal permissible level of mercury in uncontaminated sediments is <1.0mg/ kg. Sediments that were anthropogenically contaminated with mercury concentrations were significantly elevated (usually> 20.0 mg/ kg). The pearson correlation coefficient is estimated using

SN.	Heavy metal concentration	Regression equation
1	Heavy metal concentration inwater, Ennore – Arsenic	Y=-0.005X2+0.02X-0.005R <sup>2</sup> =0.90
2	Heavy metal concentration inwater, Ennore - Mercury	Nil
3	Heavy metal analysis insediment, Ennore - arsenic	Y=1.41X2-5.25X+4.23R <sup>2</sup> =0.88
4	Heavy metal analysis insediment, Ennore - mercury	Y=0.04X2-0.21X+0.35R <sup>2</sup> =0.22
5	Heavy metal concentration inwater, CFH-Arsenic	Y=-0.005X2+0.02X=0.005R <sup>2</sup> =0.90
6	Heavy metal concentration inwater, CFH - Mercury	Y=-0.005X2+0.031+0.04R <sup>2</sup> =0.93
7	Heavy metal analysis in sediment,	Y=-0.03X2-0.13X+0.27
	CFH - arsenic	$R^2=0.14$
8	Heavy metal analysis insediment, CFH - mercury	Y=1.41X2-5.25X+4.23R <sup>2</sup> =0.88
9	Heavy metal concentration infish tissues – Arsenic -I quarter	Y=-3.58X2+34.92X-35.60R <sup>2</sup> =0.76
10	Heavy metal concentration infish tissues – mercury - I quarter	Y=-0.02X2+0.19X+0.12R <sup>2</sup> =0.35
11	Heavy metal concentration infish tissues – Arsenic -II quarter	Y=2.23X2-13.09X+21.47R <sup>2</sup> =0.71
12	Heavy metal concentration infish tissues – mercury - II quarter	Y=0.03X2-0.27X+0.94R <sup>2</sup> =0.08

Table 5. Heavy	metal	concentration	and	regression	equations
				- 0	

SPSS-16.0 version. Hg, I quarter and Ar.I quarter, r=0.67, Hg, I quarter and Hg, II quarter, r=0.34, Hg, I quarter and Ar, II quarter, r=0.39, Ar, I quarter and Hg, II quarter, r=(-0.23), Ar, I quarter and Ar, II quarter, r=0.67 and Hg, II quarter and Ar, II quarter, r=(-0.12). The coefficient of variation ranged between 0.05 to 10.39%. Fig. 1 shows the contour plot of mercury and arsenic in consecutive 12



Fig. 1. Contour plot of mercury and arsenic in consecutive 12 months



Fig. 2. Three dimensional plot of mercury and arsenic in consecutive 12 months

months, Fig. 2 shows the three dimensional plot of mercury and arsenic in consecutive 12 months, Fig. 3 represents the surface plot of mercury and arsenic in the first quarter, Fig. 4 represents the surface plot of mercury and arsenic in the second quarter, Fig. 5 represents the time series plot of arsenic and mercury concentration and Fig. 6 represents the time series plot of mercury concentration.



**Fig. 3.** Surface plot of mercury and arsenic in the first quarter



Fig. 4. Surface plot of mercury and arsenic in the second quarter



Fig. 5. Time series plot of arsenic and mercury concentration



Fig. 6. Time series plot of mercury concentration

During summer months in the 2<sup>nd</sup> quarter, the arsenic value was slightly higher than other quarters in the water samples tested (0.02). This may be due to the accumulation of more toxic metals in the summer season. This coincided with the earlier findings of Agatha. Nwabueze, 2011. These higher values may also be due to anthropogenic emissions. The correlation coefficient between selected two different quarters in fish tissues were 0.64 and between 2 different metals were 0.04. The correlation coefficient between sediment and fish tissues for the metal mercury was 0.25 and for the metal arsenic was 0.14. The correlation coefficient between two quarters for the metal mercury was 0.54 and the metal arsenic was 0.32. the correlation coefficient between 2 metals viz. mercury and arsenic was much lower in fish tissues because the arsenic values were much higher than mercury but these high values of arsenic was within the WHO prescribed limits.

### CONCLUSION

The peak occurs at 7th species (Loligo sp.) for arsenic value of 45ppb and mercury value of 0.78ppb. The peak value of arsenic occurs at 60ppb at mercury concentration of 1.20ppb at second quarter. The peak arsenic values occurred in the month of May'09 and the peak mercury values occurred in the month of Sep'09. The lowest mercury and arsenic value occurred in the month of Jan'09. Mercury is much lower than the arsenic value. The mercury concentration increases for every month during the year. The peak occurs in the month of Sep'09 at a mercury concentration of 1.30ppb. The peak occurs in the month of May'09 for arsenic value of greater than 60ppb. The peak value of arsenic occurs at 60ppb at mercury concentration of 0.61ppb at second quarter.

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