*International Research Journal of Environment Sciences*_____ ISSN 2319–1414
Vol. **2(7),** 69-75, July **(2013)** *Int. Res. J. Environment Sci.*

Evaluation of the Range of Heavy Metal concentration and its levels of Accumulation in the Fish Sample of River Savitri at Mahad-MIDC, MS, India

Chavan Nilesh S.[1*] and Jawale Chetan S.[2]
[1*]Department of Zoology, G.E. Society's, Art's, Commerce and Science College, Shriwardhan, Dist. Raigad, MS, INDIA
[2]PG Department of Zoology, G.E. Society's, HPT Arts and RYK Science College, Nasik- 5, MS, INDIA

Available online at: www.isca.in
Received 22nd September 2012, revised 25th January 2013, accepted 10th May 2013

Abstract

The use and dispersion of heavy metals has increased vastly during the 20th century and the behavior of metals in the aquatic environment is therefore a matter of rising concern. Metals like all elements are not biodegradable and it can be transformed from one chemical state to another state.The effect of heavy metals pollution and accumulation of heavy metals in the Fishes have been studied with the view to check its ill effects. Sampling method was used for the study. The Water samples of River Savitri, (Taluka-Mahad, District-Raigad, M.S.) were collected from pre-defined 11 sampling points, upstream and downstream. including Mahad MIDC region to check the range of metal pollutants. One of the sampling sites was selected in upstream region, far away from Mahad MIDC to check the existence of metal pollutants in the river water before its flow through Mahad MIDC area. The site where maximum concentration of all the pollutants was observed was considered as Potent site. 11 sites studied under the sample survey. The sampling site number 9 (Mahad MIDC) shows excessive range of heavy metals compared to other upstream site number 8 and further still lesser at site number 10 in the downstream area of river Savitri. Rest of the sites, under study show the upward stream area where heavy metal range is either within tolerable range or not detected. This shows that Mahad MIDC site number 9 is the Potent site for heavy metal contamination. Water samples in triplicates were collected from Potent site every month during study to heavy metals concentration. However fish samples were tested during July, January and March to check the accumulation level of heavy metals in different seasons. During the Monsoon season i.e. July to September, the heavy metals range are above normal range when compared with Standards.. The analytical study shows that the presence of heavy metals concentration are more in the month of July and further decreasing in the month of September indicating that the untreated industrial effluents are released directly in the River water or even after treatment of industrial effluents at CEPT plant, there exist elevated range of heavy metals in river water. and this itself suggest that there is some problem with the CEPT plant functioning. Fish samples were collected during three different seasons to check the concentration of heavy metals. The analysis have shown that fish samples also have heavy metal range above normal range. Heavy metals like Zinc, Iron are essential, even Fluoride is equally important, but analyses have shown that all these elements have accumulated in the fish body indicating a chance that the accumulated heavy metals can easily enter the Food chain. The results have been discussed in the Research Project.

Keywords: Water quality, heavy metal pollution, bioaccumulation.

Introduction

Water resources are being used by human being for various purposes like agriculture, industries, hydropower, fisheries and recreational uses. At present the quality of water largely under threat due to releases of municipal, industrial, domestic and sewage wastes in the surface and ground water reservoirs[1,2].

Concentration of bio-available metals such as Arsenic, Cadmium, Chromium, Copper, Nickel, Manganese, Titanium and Zinc, Mercury and Lead is toxic to biological systems. Metals such as arsenic, lead, cadmium, mercury, and selenium are highly toxic even in minor quantities. Elevated metal concentration in the environment has a wide ranging impact on animals, plants and microbial species. Other Pollutant such as Fluoride though essential, excess of it may lead to ailments of teeth and bones[3]. Heavy metal and their salts are considered as very important group of environmental pollutant which in small quantities maybe essential nutrients that protect your health, yet in larger quantity it become toxic and dangerous to human being[4].

River Savitri is an important river flowing through Ratnagiri and Raigad districts of Maharashtra State. It is a major source of water for domestic usage, agriculture and industrial purposes in these districts. Raigad district is geographically subdivided into three parts as, the sea coast, the central belt and the hilly areas of Sahyadri range. The mainstream industrial developments in this district have been made mainly in the vicinity of the rivers. Industrial development in Raigad district has accelerated since

1970 due to the prohibition of industrial establishment in the nearby Mumbai metropolitan. The population of Mahad Maharashtra Industrial Development Corporation MIDC is18662[5].

The River Savitri originates from the mountains at Mahabaleshwar and flows towards Poladpur and meets to creek after Mahad town. After Mahad, towards the Arabian Sea, the creek is known as Bankot creek. The water is supplied from this river to Navenagar of Mahad, the industrial estate and to some nearby villages. Majority of the industrial units established in these areas are chemical factories. There are 27 factories, of which 7 manufacture Dyes and Dye intermediates and Pharmaceutical, 18 industries are of Drugs and Pharmaceuticals, 1 deals with petrochemical and 1 deals with paper and pulp industry. 6 industries are closed. Almost all are fall under Red Category. All the effluents are disposed in the river Savitri[6].

Possible reasons of the pollution: i. Accidental discharges of effluents directly or indirectly from the Industries, ii. Unauthentic disposal of solid waste at the bank of river and vicinity which may find way into the river in rainy season, iii. Lack of proper Operation and Maintenance as well as upgradation of Effluent Treatment Plant. iv. Use of explosives or other poisonous chemicals at many places. v. Washing of chemical tankers in the river at many places. vi. Domestic waste water of city is a major source of pollution. vii. Discharge of Domestic waste from Mahad MIDC is a regular and substantial source of river pollution. viii. Agricultural wash out may cause pollution of river water.

Objectives of the study: i. To study the chemical composition and water quality parameters of Savitri River. And to investigate the possible sources and Cause of pollution in the area, ii. To investigate the Environmental impact of possible effluent pollution by analyzing chemical composition and heavy metal contents in certain forms of Fishes, iii. To study if these effects can be attributed to the change in the chemical composition of the river water. iv. The present study will investigate the effects of heavy metals on the health status of the population residing in the nearby villages of river Savitri, of the Mahad MIDC considering that the presence of heavy metal toxicity of river has adversely affected the ecological balance. In eco-toxicity studies, vertebrate organisms like fish could act as a bio-indicator of fresh water contamination of heavy metals and its adverse effect on the nearby community.

Material and Methods

Sampling method was used for the study. Water Samples during whole study period were collected from November 2006 and January 2007 to December 2007 to study Physico-Chemical parameters and Concentration of heavy metals. Water samples were collected in triplicate from total 11 different sampling sites within Mahad taluka, from upstream and downstream of the Savitri River including Mahad MIDC to check the concentration of various heavy metals like Arsenic, Cadmium, Nickel, Zinc, Iron as well as the concentration of fluorides. The potent site was selected among the 11 sampling sites . It was observed that the potent site at Mahad-MIDC exhibited highest concentration of heavy metals and fluorides, it was considered as the "Potent Site". Among rest of the sampling sites, one of the sites at upstream of the Savitri River exhibited lowest range of metal concentration and was considered as the "Controlled Site"

The Fish species *Mugil cephalus*, as a member of river fauna was used to analyse accumulation of heavy metals in three sets of ten fishes each during the year from January-2007 to December-2007 in alternate month. The Fishes were digested and these digested Fish Samples in triplicate were analyzed to check the accumulation of heavy metals using a flame atomic absorption spectrophotometer in a commercial laboratory.

Metal analysis was done by AA 100 - Atomic Absorption Spectrophotometer (Perkin Elmer, USA) at parts per million (ppb) level. The heavy metals having notable readings in the AAS were further subjected to analysis using AA 400 -AAS graphite (Perkin Elmer, USA) at parts per billion (ppb) level.

1 ml sample was digested completely by addition of 1 ml concentrated HCl and Concentrated HNO_3, each. To this 30 ml distilled water was added. For AA 400, ultra pure water was used[5]. The solution was heated on a hot plate for 30 minutes. Digested sample was filtered through Whatman filter paper. Filtrate was diluted up to desired volume. Appropriate hollow cathode lamp was used as per the element under investigation[7,8].

The metal contaminants in aquatic systems usually remain either in soluble or suspension form and finally tend to settle down to the bottom or are taken up by the organisms. The progressive and irreversible accumulation of these metals in various organs of marine creatures ultimately leads to metal-related diseases in the long run because of their toxicity, thereby endangering the aquatic biota and other organisms Fishes being one of the main aquatic organisms in the food chain, may often accumulate large amounts of certain metals[9]. Essentially, fishes assimilate these heavy metals through ingestion of suspended particulates, food materials and/or by constant ion-exchange process of dissolved metals across lipophilic membranes like the gills/adsorption of dissolved metals on tissue and membrane surfaces.

The fish samples were washed with clean fresh water, brought to the laboratory in an icebox. The samples were measured (size ~1 mm and weight ~1 g), dissected with clean equipment and then freeze-dried for 48 h. The muscles of the all fishes were pooled and placed in 30 g small plastic vial separately. On each occasion, samples were collected in three replicate spots at each station and the mean values recorded. The fish samples were caught with nets and traps. The fish samples after defrosting were dissected and oven-dried to constant weight at 105 ± 20°C and were each ground to powder. The powdered samples were digested[10]. 1 g of each sample was digested using 1.5.1 mixture of 70% perchloric acid, concentrated nitric acid and

concentrated sulphuric acid at 80 ± 5°C in a fume chamber, until colorless liquid was obtained. Each digested sample was made up to 20 ml with de-ionized water and analysed for Arsenic, Cadmium, Iron, Nickel and Zinc by Inductively Coupled Plasma Atomic Emission Spectrometer (Perkin Elmer Optical Emission Spectrometer). All digested samples were analysed three times for metals. Analytical blanks were run in the same way as the samples and concentrations were determined using standard solutions prepared in the same acid matrix[11]. Values of heavy metals were recorded in mg/kg.

The Fluoride content was analyzed by colorimetric method by using Alizerin dye as an indicator. Sets of test tubes were prepared by taking standard Fluoride solution of variable concentrations. Alizerin dye was added in each test tube and the optical density (OD) was measured with 420nm radiation. The standard graph was prepared. Sample water was also treated with Alizerin dye. OD was measured and the Concentration was measured by using standard graph[11].

Table-1
Showing concentration of heavy metals and Fluoride at 11 different sites

Metals	Site-1 Metal Concentration Mean ± SD	Site-2 Metal Concentration Mean ± SD	Site-3 Metal Concentration Mean ± SD	Site-4 Metal Concentration Mean ± SD	Site-5 Metal Concentration Mean ± SD
Arsenic ppb	-	-	-	-	-
Nickel ppb	-	-	-	0.0374 ± 0.002	-
Cadmium ppb	0.0049 ±0.0003	0.0042 ± 0.0001	-	0.0118 ± 0.02	0.077 ± 0.002
Zinc ppb	0.0044 ± 0.002	0.0038 ±0.001	-	0.0043 ± 0.01	0.0695 ± 0.03
Flouride ppb	0.1059 ±0.05	0.1511 ±0.08	0.3798 ± 0.0002	0.0066 ± 0.004	0.0096 ± 0.03
Iron ppb	0.0436 ±0.03	0.0365 ± 0.06	0.0173 ± 0.2	0.172 ± 0.1	0.05 ± 0.03

Metals	Site-6 Metal Concentration Mean + SD	Site-7 Metal Concentration Mean + SD	Site-8 Metal Concentration Mean + SD	Site-9 Metal Concentration Mean + SD	Site-10 Metal Concentration Mean + SD	Site-11 Metal Concentration Mean + SD
Arsenic ppb	-	-	0.5 + 0.05	1.25 + 0.08	-	-
Nickel ppb	-	-	0.1047 + 0.0003	0.1309 + 0.002	0.00735 + 0.18	-
Cadmium ppb	-	-	0.0105 + 0.2	0.014753 + 0.25	0.0082 + 0.003	-
Zinc ppb	-	-	0.098 + 0.2	0.137693 + 0.22	0.0074 + 0.29	-
Flouride ppb	0.0033 + 0.0002	0.0196 + 0.0002	0.2115 + 0.7	0.5288 + 0.7	0.297 + 0.104	-
Iron ppb	0.047 + 0.02	0.069 + 0.03	0.0511 + 0.2	0.1278 + 0.3	0.0718 + 0.3	0.026 + 0.02

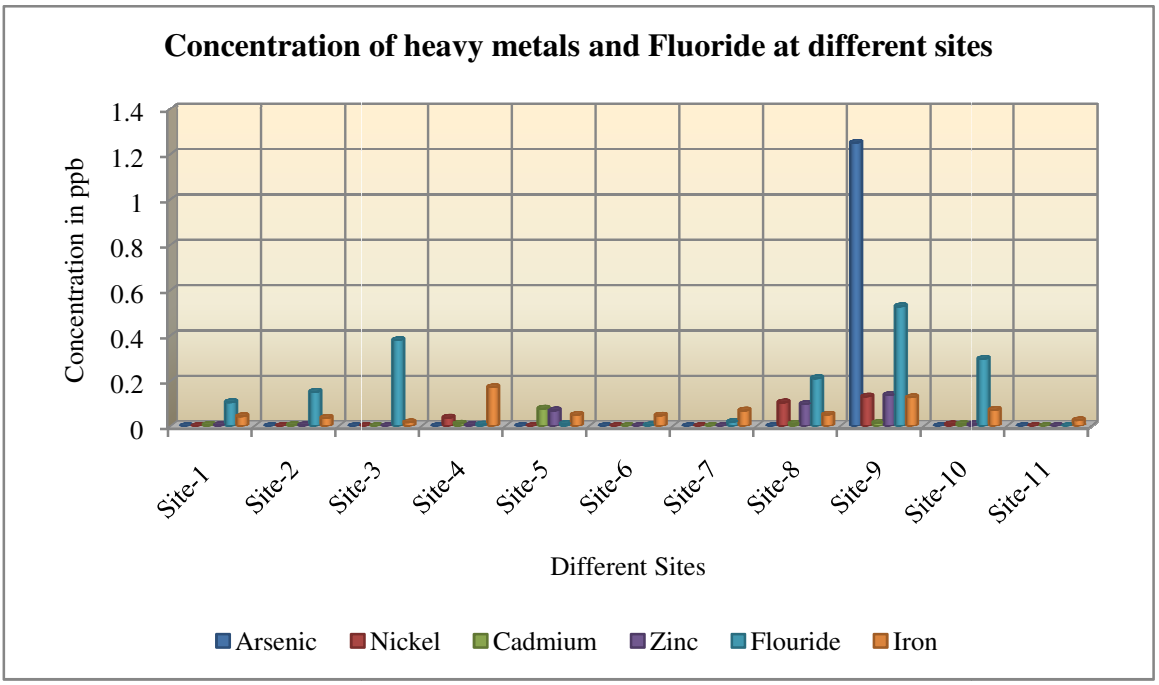

Figure-1
Showing concentration of heavy metals and Fluoride at 11 different sites

Table -2
Showing Heavy Metal Analysis of Water collected from potent site

Prameters	**January Mean ± SD**	**February Mean ± SD**	**March Mean ± SD**	**April Mean ± SD**	**May Mean ± SD**	**June Mean ± SD**
Arsenic ppb	-	-	-	-	-	2.5 ± 0.2
Nickel ppb	0.0436 ± 0.0008	0.0374 ± 0.0003	0.094 ± 0.003	0.1047 ± 0.606	0.069 ± 0.007	0.26175 ± 0.001
Cadmium ppb	0.0049 ± 0.0003	0.0042 ± 0.0002	0.0105 ± 0.0008	0.0118 ± 0.0002	0.077 ± 0.0015	0.0295 ± 0.0004
Zinc ppb	0.0044 ± 0.0005	0.0038 ± 0.0003	0.0096 ± 0.0002	0.0106 ± 0.0002	0.0695 ± 0.0004	0.0265 ± 0.0005
Flouride ppb	0.1059 ± 0.0002	0.1511 ± 0.0001	0.3798 ± 0.0014	0.423 ± 0.0002	1.0575 ± 0.52	2.788 ± 0.0012
Iron ppb	0.0436 ± 0.0001	0.0365 ± 0.0005	0.0917 ± 0.0002	0.1022 ± 0.0002	0.2555 ± 0.0006	0.674 ± 0.003
Prameters	**July Mean ± SD**	**August Mean ± SD**	**September Mean ± SD**	**October Mean ± SD**	**November Mean ± SD**	**December Mean ± SD**
Arsenic ppb	5.0 ± 0.01	5.0 ± 0.01	1.0 ± 0.4	-	-	1.5 ± 0.3
Nickel ppb	5.65 ± 0.418	5.0 ± 0.6	1.047 ± 0.005	0.00735 ± 0.0008	0.0674 ± 0.0008	0.15705 ± 0.0002
Cadmium ppb	5.0 ± 0.416	5.0 ± 0.2	0.118 ± 0.003	0.0082 ± 0.0003	0.0075 ± 0.0003	0.0177 ± 0.0002
Zinc ppb	4.33 ± 0.2	6.44 ± 0.3	0.106 ± 0.003	0.0074 ± 0.0003	0.0068 ± 0.0002	0.0159 ± 0.0003
Flouride ppb	65.78 ± 0.12	66.58 ± 0.115	4.23 ± 0.04	0.297 ± 0.002	0.272 ± 0.002	0.6345 ± 0.0005
Iron ppb	10 ± 0.272	10 ± 0.153	1.022 ± 0.002	0.0718 ± 0.0001	0.0066 ± 0.002	0.4044 ± 0.0006

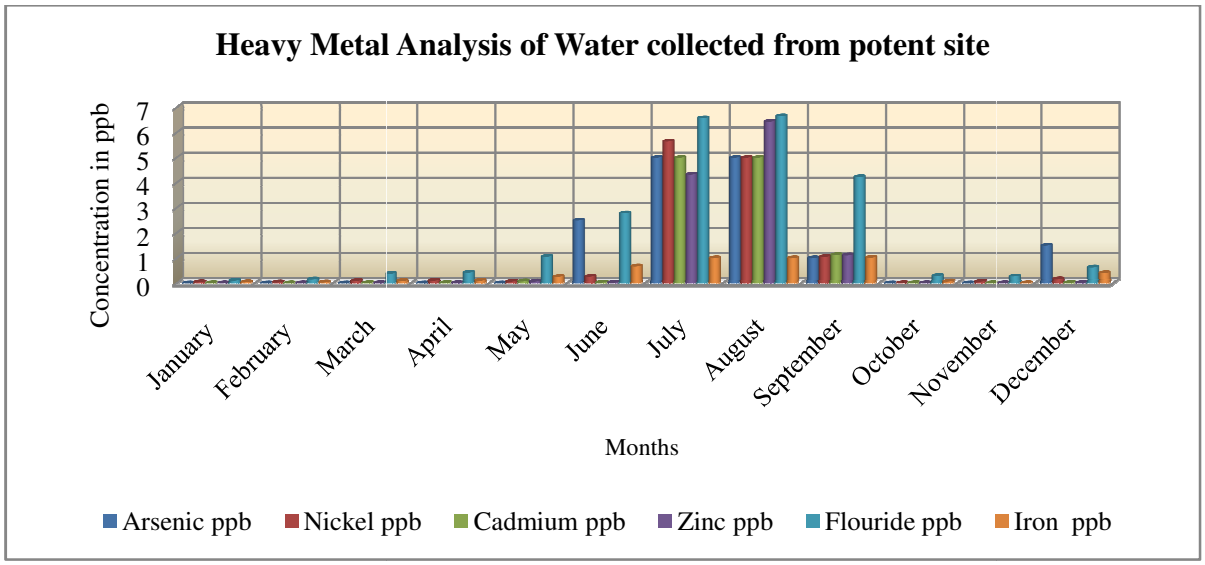

Figure-2
showing Heavy Metal Analysis of Water collected from potent site

Table-3
Showing Heavy Metal Analysis of Fish Sample

Sample No.	Fish Sample 1Mean±SD	Fish Sample 2 Mean±SD	Fish Sample 3 Mean±SD	Fish Sample 4 Mean±SD	Fish Sample 5 Mean±SD	Fish Sample 6 Mean±SD
↓Metals →Months	January	March	May	July	Sep	Nov
As(ppb)	0.197±0.01	N.D.	N.D.	N.D.	N.D.	2.05± 0.05
Ni(ppb)	0.54± 0.02	0.59± 0.04	0.557± 0.03	0.74± 0.31	0.787±0.008	0.764± 0.02
Cd(ppb)	0.32±0.005	N.D.	N.D.	N.D.	N.D.	0.57± 0.002
Zn(ppb)	0.486± 0.1	0.473± 0.32	0.42± 0.3	0.57± 0.32	0.582± 0.001	0.562± 0.91
Fl(ppb)	1.57± 0.2	1.51± 0.22	1.548±0.01	1.02± 0.02	1.59± 0.03	1.034± 0.03
Fe(ppb)	0.278± 0.02	0.296±0.02	0.401±0.09	0.41±0.18	0.396±0.006	0.367±0.06

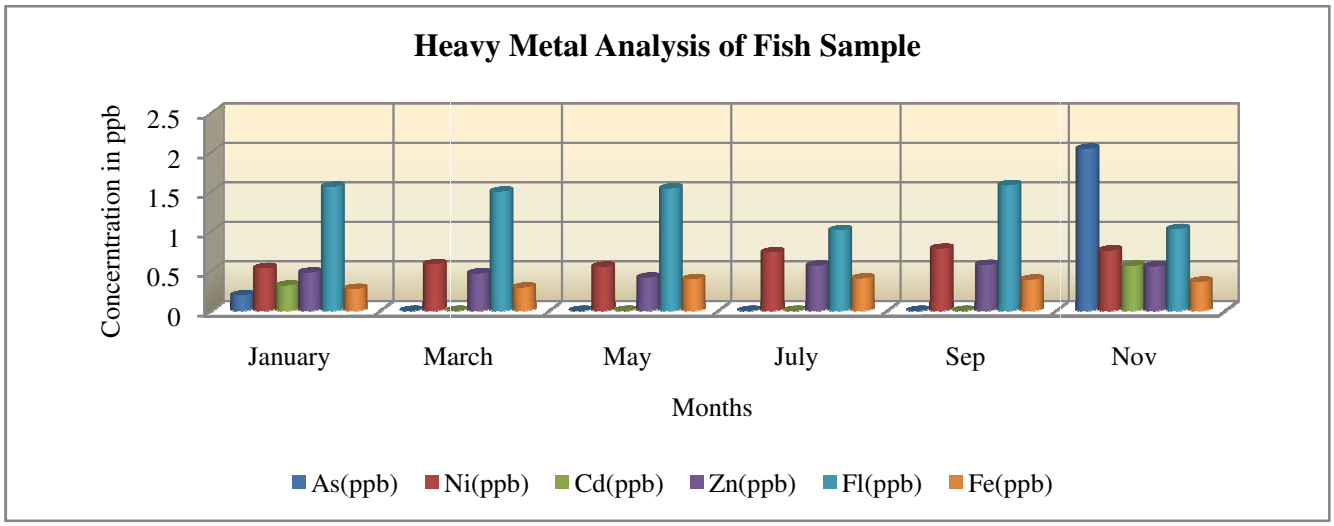

Figure-3
Showing Heavy Metal Analysis of Fish Sample

Table-3
Showing Maximum and Minimum range of heavy metal concentration in water and fish sample

Sr. No.	Parameters	Maximum Range(ppb)		Minimum Range(ppb)		Permissible Range
		Water	Fish	Water	Fish	
1	Arsenic	5.0 ± 0.01	2.05 ± 0.05	1.5 ± 0.3	1.97 ± 0.01	0.01
2	Cadmium	5.0 ± 0.418	0.57 ± 0.002	0.004 ± 0.0002	0.32 ± 0.005	0.003
3	Nickel	5.65 ± 0.416	0.787 ± 0.08	0.0074 ± 0.001	0.54 ± 0.02	0.07
4	Zinc	6.44 ± 0.295	0.582 ± 0.001	0.004 ± 0.0003	0.442 ± 0.3	5.0
5	Iron	1.0 ± 0.27	0.41 ± 0.09	0.007 ± 0.002	0.3278 ± 0.02	0.3
6	Fluoride	6.658 ± 0.12	1.59 ± 0.03	0.1059 ± 0.0002	1.02 ± 0.09	1.5

Results and Discussion

During this investigation, 11 sites studied under the sample survey referred in the table, the sampling site number 9 (Mahad MIDC) shows excessive range of heavy metals compared to site number 8 and further still lesser at site number 10 (Birwadi) in the downstream area of river Savitri. Rest of the sites, under study show the upward stream area where heavy metal range is either within tolerable range or not detected. The conclusion arrived at shows Mahad MIDC site number 9 as the Potent site for heavy metal contamination.

During the Monsoon season i.e. July to September, the physico-chemical parameters as well as range of heavy metals are above normal limits when compared with WHO standards[12-14]. The analytical study shows that the presence of physico-chemical parameters and heavy metals concentration are more in the month of July and further decreasing in the month of September. This means that the untreated industrial effluents are released directly in the River water or even after treatment of industrial effluents at Common Effluent Treatment Plant CETP, there exists elevated range of heavy metals in river water. This itself suggests that there is some problem with the functioning and efficacy of CETP.

Fish samples were collected every alternate month to check the concentration of heavy metals. The analysis has shown that fish samples also have heavy metal levels above normal limits. Heavy metals like Zinc, Iron are essential, even Fluoride is equally important[15], but analyses have shown that all these elements have accumulated in the fish body and the conclusion arrived at shows that there exists a chance of the accumulated pollutants easily entering the Food chain.

The Fluoride toxicity of water at Mahad MIDC site was the highest due to untreated discharge of Industrial wastes. High concentrations of Zinc, Iron, Cadmium and Nickel were reported in the river Ravi and ground waters of Hydrabad[16,17].

The magnitude of heavy metals concentration in the river Savitri is F>Zinc>Ni>As>Cd>Fe. The occurrence of heavy metals in the aquatic habitats is dependent upon wide range of chemical, biological and environmental factors[18,19].

Conclusion

It is assumed that this information will definitely help to form the basis and foundation of future work. There is considerable scope for further studies to achieve final goal of qualitative and quantitative evaluation of the existence of the pollution.

References

1. Pathak Neelam B. and Mankodi P.C., Hydrological status of Danteshwar pond, Vadodara, Gujarat, India, *International Research Journal of Environment Science,* **2(1),** 43-48 **(2013)**

2. Gautam A., Ecology and pollution of mountain water: A case study of Bhagirathi River, Ashish Publishing House, New Delhi, 209 **(1990)**

3. Järup L., Hazards of heavy metal contamination. British Medical Bulletin, **68**, 167-182 **(2003)**

4. Kapoor Neeti and Tiwari Prakash, Effects of Heavy Metal Poisoning during Pregnancy, *International Research Journal of Environment Science,* **2(1),** 88-92 **(2013)**

5. www.wikipedia.org/mahad-midc **(2013)**

6. http://www.mpcb.mah.nic.in MPCB Report 2004-2005 **(2013)**

7. Greenberg, A.E., Clesceri, L.S. and Eaton, A.D , Standard Methods for Examination of Water and Waste Water, *APHA publ, 21st edition,* APHA, Washington DC, USA **(1992)**

8. Sah R.N. and Miller R.O., Spontaneous reaction for acid dissolution of biological tissues in closed vessels', *Anaytical Chemistry*, **64**, 230-233 **(1992)**

9. Trivedi R.K. and Goel P.K., Chemical and Biological Methods for water pollution studies, *Environmental publication*, corrected reprint 1986, **(1986)**

10. Sharma M.R., Assessment of Ground Water Quality of Hamirpur Area in Himachal Pradesh, *Pollution Research,* **23(1),** 131–134 **(2004)**

11. Vogel's textbook of *Quantitative Chemical Analysis*, Denney,Barnes,6th edition, Pearson publication **(2006)**

12. WHO, Lead, *Environmental Health Criteria*, 165, Geneva: World Health Organization, **(1995)**

13. WHO, Arsenic and Arsenic Compounds. *Environmental Health Criteria,* vol. 224, Geneva: World Health Organization, **(2001)**

14. http://www.waterstandards.com/metals.html **(2013)**

15. Javed M. and Hayat S., Effect of waste disposal on the water quality of river Ravi from Lahore to Head Baloki, *Proc. Pak Cong.Zool.*, **15**, 41-51 **(1995)**

16. Muhammad Ubedullah, Studies on heavy metal toxicity of water, sediments, plankton and fish in the river Ravi stretch from Baloki headworks to Sidhnai barrage, (pdf version, http://ethesis.485Ph.D.pdf), **(2003)**

17. Shailaja K., Johnson Mary Esther C., Heavy metals in the ground waters of same areas of Hyderabad, *Nature of Environmental Pollution Technology*, **5(3),** 447-449 **(2006)**

18. Srinivasa Gowd S. and Govil P.K., Distribution of heavy metals in surface water of Ranipet industrial area in Tamil Nadu, India, *Environmental Monitoring and Assessment,* Springer Netherlands Publication, **(2007)**

19. Tiwari A.K., Dikshit R.P., Tripathi I.P. and Chaturvedi S.K., Fluoride content in Drinking water and ground water quality in rural area of tahsil Mau, district Chitrakoot , *Indian J. Environmental Protection,* **23(9),** 1045-1050 **(2003)**