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Status of Heavy metal pollution in Mithi river: Then and Now

Shruti Handa and Rahul Jadhav
Vidyavardhini's
A.V College of Arts, K.M College of Commerce and E.S.A College of Science, Vasai Road.401 202.
(Maharashtra), INDIA.

Abstract: The Mithi River runs through the heart of suburban Mumbai. Its path of flow has been severely damaged due to industrialization and urbanization. The quality of water has been deteriorating ever since. The Municipal and industrial effluents are discharged in unchecked amounts. The municipal discharge comprises untreated domestic and sewage wastes whereas the industries are majorly discharge chemicals and other toxic effluents which are responsible in increasing the metal load of the river. In the current study, the water is analysed for heavy metals- Copper, Cadmium, Chromium, Lead and Nickel. It also includes a brief understanding on the fluctuations that have occurred in the heavy metal pollution, through the compilation of studies carried out in the area previously.

Key words: Heavy metals, Mithi River, Pollution, Industrialization

I. Introduction

Rivers all over the world play a very significant role. They have been an important source of fresh water since ages, for irrigation, agriculture, drinking etc. As we progressed water has also accommodated our needs of electricity generation through hydropower, which has made further developments possible. As our needs kept growing, we have forgotten to acknowledge the worth of the water bodies. The rapid growth in population and subsequent industrialisation has led to discharge of unimaginable amount of pollutants discharged into water bodies. The contribution to pollutants from illegal small scale industries on the banks of most rivers is also dangerous. Industries involved in dyeing, tanning, printing etc. add to the amount of existing pollutants in the water body. Fertilizers, insecticides and pesticides also add to the water pollution by leaching. Thus as the river meanders through its course, it receives a heavy load of effluents from industries as well as pollutants from anthropogenic activities. Some of the major causes of heavy metal in the rivers are flawed industrial processes, discharge of industrial effluents containing untreated metallic solutions, dumping of solid wastes containing metal salts and some agricultural practices using metal based biocides (Anand and Pandey, 2014).

Heavy metals are present on the earth's crust and our naturally present in the water bodies. In normal concentrations they are useful to the biota. They are of high density and can be toxic when the concentrations rise above the normal level. The presence of heavy metals in industrial effluents is known to have major hazard to natural water, animal and human health. High concentrations all of heavy metals have deleterious effect on the environment (Cheng, 2003). Random developments in industrialization have a heavy impact on the environment; the untreated industrial waste water discharged to the nearby water bodies may cause severe ground water pollution (Gleick, 2014). Additionally, it increases the heavy metal concentrations in water manifold causing severe consequences to life. Due to rapid industrialization over the past century, heavy metals have been discharged into the major rivers and estuaries of the world (Tam and Wong, 2000;Cobelo-Garcia and Prego, 2003; Chen *et. al.*, 2004; Pekey, 2006) Rivers make a major contribution of metals in the marine environment and are considered as a dominant pathway for metals transport (Harikumar *et.al.*, 2009). During their transport, the heavy metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Akcay *et. al.*, 2003, Abdel-Ghani and Elchaghaby, 2007). Metals are non-degradable and causing damage to nervous system and internal organs (Kar *et. al.*, 2008; Lee. *et. al.*, 2007). Rivers in Mumbai are in a highly deteriorated state. A number of regulations and efforts have been implemented and scraped. Mithi River has been a huge example to the rampant development in the city. Developments in the form of new small scale industries, slums etc. pile up over its banks. The objective of the current investigation is to understand the changes that have occurred in the heavy metal concentrations present in the downstream areas of Mithi River measuring a span of 05-10 years.

The parameters for the metals Copper, Cadmium, Chromium, Nickel and Lead for the year 2013 and 2015 have been evaluated by the authors of this paper. To evaluate the status of the river from the past, parameters have been compiled from 2004(MPCB) and 2010- 2011(Singare *et. al.*, 2012).

II. Materials and Methods

Study area

The Mithi River begins from the overflow of Vihar and Powai lakes which lie in the pristine and protected areas of the city. It meanders its way through down through the slowly growing shanties upstream to the thickly populated banks on the downstream. The water is visually clear and odourless at its mouth but slowly turns into a black, smelly stream struggling to make its way through the slums and industries to meet the bay. The area is located along western Arabian cost of India from $18^{0.}$ 53' N to 19^0 16' N latitude and from 72^0 E to $72^0$59' longitude (Singare *et. al*., 2012). Three locations downstream were narrowed down. These locations were kept as close as possible to the studies carried out previously by MPCB Report on Mithi River (2004) Water Pollution and Recommendations for its Control and (Singare *et. al*., 2012).

Sampling and Laboratory methods

The sampling was carried out during summers to maintain uniformity with the data that was available. The study was conducted in 2013 and 2015. Water was collected in clean, autoclaved one litre plastic containers. The samples were brought to the laboratory immediately and kept at 4^0 C to maintain its condition very close to the time it was sampled. The analysis was carried out within 4 hours of water collection. The digestion was carried out by standard methods (APHA, 2005; Trivedi R.K 1988). 5ml aqua regia was added to appropriate amount of sample and was allowed to digest at around 75^0C. The volume was reduced to near dryness. Further, nitric acid was added until white residue was formed. This residue was dissolved with nitric acid. Once dissolved, it is filtered through Whatmann filter paper and the final volume is made to 100ml using distilled water.

Heavy metal analysis

The heavy metals were analysed by atomic absorption spectroscopy (Thermo Elemental, AAS Solar Series) and Inductive coupled plasma –optical emission spectroscopy, model. ARCOS, (SPECTRO). The samples were prepared in triplicates to obtain a constant result.

Heavy Metal evaluation methods

Contamination Index shows the combined effects of overall water quality parameters of an area. Different contamination index methods has been developed all over the world for groundwater quality assessment such as heavy metal indexing approach (HMI), degree of contamination (C_d), contamination factor (C_f), Metal pollution index(MPI), Pollution index (PI) etc. By using these methods, we can easily calculate the overall water quality of a particular area rapidly and efficiently because these methods present the single value by comparing different parameters (Singh *et. al*., 2015).

In order to understand the magnitude of contamination different heavy metal indices were used. The background values were supported from the data given by Central pollution control board.

The following heavy metal evaluation methods for the year 2004, 2011, 2012, 2013 and 2015, for the metals Copper, Cadmium, Chromium, Nickel and Lead have been calculated and interpreted by the authors of this paper.

Contamination Factor (C_f)

The aim of calculating contamination factor is to provide a measure of the degree of overall contamination in a sampled site. It was developed by (Hakanson, 1980). The formula is as follows:

$C_f = C/C^0$

Where, C_f is the ratio obtained by dividing the mean concentration of each metal in the sample (C) value by the baseline or background (C^0)

Degree of Contamination (C_d)

It summarises the combined effects of several parameters considered harmful to water (Backman *et. al.*, 1998). In the current study several heavy metals that were studied were analysed and the contamination index is calculated as follows:

$$C_d = \sum_{i=1}^{N} Cfi$$

$$Cfi = CA_i / CN_i - 1$$

Where,
Cfi -the contamination factor for the i^{th} component
CA_i - analytical value for the i^{th} component CN_i - upper permissible concentration of the i^{th} component (N denotes the “normative value”) (Bansal, 2014).
C_d is calculated for every sample independently, values are grouped into three categories regarding contamination level as follows: low contaminations if Cd values are lower than 1. Medium contamination when C_d is between 1 and 3. C_d is high when contamination is more than 3 (Aktar *et. al*., 2010). The degree of contamination (C_d) was used as reference to estimate the extent of metal pollution (Al-Ami *et. al*., 1987).

Metal Pollution Index (MPI)

The MPI has been used for the evaluation which shows the composite influence of individual parameters on the overall quality of water (Tamasi and Cini , 2004). Higher be the concentration of a metal as has been compared to its maximum tolerable concentration, the poorer quality of the water (Amadi, 2011).The MPI represents the sum of the ratio between the analyzed parameters and their equivalent National standard values (Chon *et. al*.,1997) as given below:

$$\sum_{i=1}^{n} [Ci/(MAC)_i]$$

Where,
C_i: mean concentration
MAC: maximum allowable concentration
The readings from the past reports were converted into appropriate values and the calculations were done accordingly for mean and standard deviation.

Statistical Analysis

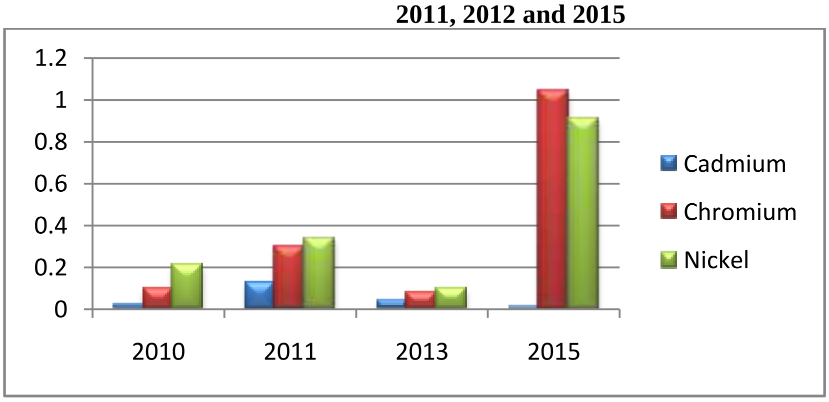
Pearson correlation (r) will be used to interpret the data since it measures the degree of linear relationship between two variables.
The statistical analysis for the year 2004, 2011, 2012, 2013 and 2015, for the metals Copper, Cadmium, Chromium, Nickel and Lead have been calculated and interpreted by the authors of this paper.

III. Result and Discussion

Table .1 Mean ± S.D. concentrations of heavy metals (mg/L) from the year 2010, 2011, 2013 and 2015

Parameters	Unit	2004	2010	2011	2013	2015	Permissible Limits (CPCB)
Cadmium	mg/L	-	0.02±0.01	0.13±0.07	0.04 ±0.02	0.01±0.003	2.0
Chromium	mg/L	NIL	0.1±0.08	0.3±0.17	0.08±0.10	1.04±0.22	2.0
Nickel	mg/L	-	0.21±0.16	0.34±0.25	0.1±0.03	0.91 ±0.21	3.0
Lead	mg/L	0.09 ±0.10	0.16±0.08	0.31±0.23	0.23±0.11	0.3 ±0.26	0.1
Copper	mg/L	0.64±0.83	-	-	0.11±0.07	0.21 ±0.03	3.0

Figure.1 Comparative graph of mean values of heavy metals (Cadmium, Chromium and Nickel) of 2010, 2011, 2012 and 2015

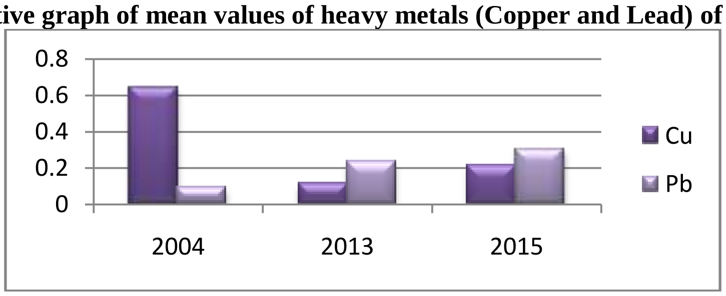


Cadmium has its most significant use in cadmium or nickel batteries. The cadmium coating provides good corrosion resistance especially in environment high stress. Cadmium is also used in pigments, stabilizers for PVC, in alloys and electronic compounds. It is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. The toxicity of cadmium originates from its chemical similarity to Zinc. It is biopersistent and once absorbed in the human body, it can get accumulated for long causing renal damage. It interferes with metabolic processes in plants and can bioaccumulate in aquatic organisms and enters in food chain (Adriano, 2001). It is also capable of causing bone defects in animals and humans. Once absorbed, cadmium irreversibly accumulates in the human body, in particularly in kidneys (Johri *et. al*., 2010), the bone and the respiratory tract (Bernard, 1986). The permissible limit of Cadmium in inland surface waters given by the CPCB (Central Pollution Control board) is 2.0 mg/L. The values of cadmium have not crossed the permissible limits in our study area. There is an increase of cadmium values in 2011 as seen in the (figure-1), but its level seems to be controlled in 2015.

Chromium is used in pigments for paints, cement, paper, rubber etc. They are also used in metal alloys. A long term exposure to chromium can cause damage to lungs and intestinal tract. Besides the lungs and intestinal tract, the liver and kidney are often target organs for chromate toxicity (Rom, 2007). It also has the potential to have negative effects on the circulatory and nerves tissues. It is known to have visible effects through bioaccumulation thus causing the danger of eating fish which must have been exposed to high levels of chromium. It shows a high increasing trend from the year 2010 to 2015(figure -1). Although a fall in its level is visible in 2013. The permissible limit given by CPCB is 2.0 mg/L for total Chromium. The values are within the limits but a high increase is visible through the years.

Nickel is used in electroplating, steel industries, ceramics, storage batteries, dyeing etc. It can be toxic to aquatic organisms such as reduction in skeletal calcification and diffusion capacity of gills (Moore, 1991). Its long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. Its bioaccumulation capacity is not very clear. Nickel compounds have been well established as carcinogenic in many animal species and by many modes of human exposure but their underlying mechanisms are still not fully understood (Clayton and Clayton, 1994, Chang, 1996). The permissible limit given by CPCB is 3.0 mg/L. As observed in (figure-1), there is an increase in concentration from 2010 to 2015 with a fall seen during the year 2013. The concentration does not exceed the standard permissible limits, but an increase is evident with each passing year.

Figure.2 A comparative graph of mean values of heavy metals (Copper and Lead) of 2004, 2013 and 2015



Copper is used in mining, metal production, storage batteries and fertilizer production industries. A long time exposure to copper can cause anemia, liver and kidney damage. It can also lead to stomach and intestinal irritation. The permissible limit suggested by CPCB for copper is 3.0 mg/L. The concentrations of copper in our study area does not show exceeding amount of the element. A decade before in 2004 before the Mithi river deluge, it was seen in an exceedingly risen amount by 2013 it has reduced. In 2015 an increase in concentrations as compared to 2013 is seen (Figure 2).

Lead due to its physical and chemical properties is used in the manufacturing, construction and chemical industries. It is also used in batteries, petrol additives, alloys, pigments and compounds. The above are few listed uses of lead. Its exposure has negative effects on neuropsychological developments in children. The permissible limit for lead suggested by CPCB is 0.1. The concentration of lead in our study area shows an increase in 2013 and in 2015 there is further rise in the levels of lead rise as compared to the MPCB report(2004)(Figure. 2)

Table. 2 Metal pollution Index (MPI) and Degree of Contamination (C_d) (Copper and Lead only) 2004, 2013 and 2015

Year	MPI	C_d
2013	1.18	1.64
2015	1.57	3.07

Table.3 Metal pollution Index (MPI) and Degree of Contamination (C_d) (Cadmium, Chromium, Nickel and Lead) 2010, 2011, 2013 and 2015

Year	MPI	C_d
2010	0.45	-2.84
2011	0.94	3.13
2013	0.62	-0.58
2015	1.11	3.98

The Metal Contamination Index (MPI) values of samples calculated for the year 2004 was 0.66. The calculated values for 2013 and 2015 are represented (Table.2) for the heavy metals Lead and Copper. A clear increase in the mentioned heavy metals can be observed, suggesting a decrease in the quality of water.
The MPI, values for the heavy metals Cd, Cr, Ni and Pb in the year 2010 and 2011 was 0.45 and 0.94 respectively. The increase in the value suggests degradation of the quality of water from 2010 to 2011. In the year 2013 and 2015 the MPI values have increased implying further deterioration in the water quality (Table.3)
The Degree of Contamination (C_d) of the sample taken in the year 2010 and 2011 is -2.84 and 3.13 respectively. The values for the samples taken in 2013 and 2015 are shown in Table 3.The degree of contamination is less than 1 in 2010 and more than 3 in 2011 suggesting that the degree of contamination is less in 2010 while it is high in 2011.The above values summarise the contamination for Cadmium, Nickel, Chromium and Lead only.
C_d of the water samples calculated for 2004 is -0.98. The C_d for 2013 and 2015 is represented in the (Table .2). The above values summarise the contamination for Copper and Lead only. The C_d of water samples contaminated with Copper and Lead is less than 1 in 2004 implying less contamination. It is between 1-3 in 2013 showing medium contamination, while it is more than 3 in 2015 which shows high contamination.

Table. 4 Contamination Factor (C_f)

Year/Heavy Metals	Cu	Cd	Cr	Ni	Pb
2013	0.03	0.02	0.04	0.03	2.3
2015	0.07	0.005	0.52	0.30	3

The contamination factor of Lead calculated for the year 2004, 2010 and 2011 is 0.9, 1.6 and 3.1 respectively. The values calculated for Copper for the above mentioned years is 0.21, 0.03 and 0.07. There is an increase in the individual factors for lead but a decline is observed in the values calculated for copper from 2004 to 2010. The values of copper show an increase from 2010 to 2011. The values for 2013 and 2015 have been shown in the (Table.4). Thus values of copper have been less than 1 all throughout, with an increase within the range. Lead has shown a constant increase as a contamination factor.

The contamination factor for Cadmium, Chromium, Nickel and Lead calculated for the year 2010 is 0.01, 0.05, 0.07 and 1.6 respectively. The factor for the above mentioned heavy metals in the year 2011 is 0.06, 0.15, 0.11 and 3.1.The values for the contamination factor in 2013 and 2015 is shown (Table.4). The values of Cadmium, Copper and Nickel show an increase in all the years except 2013. Lead values have risen consistently. It is higher than the Copper, Cadmium, Chromium and Nickel. It is higher than 1 in all the years i.e. from 2010 to 2015. In the year 2004, it was close to 1. In 2010, (Pb > Ni > Cr > Cd), 2011(Pb > Cr > Ni > Cd), 2013(Pb > Cr > Ni > Cu > Cd), 2015(Pb > Cr > Ni > Cu > Cd). Thus, an increase is observed in the contamination factor from the past decade till today. Similar observation with regard to Lead was made by (Akhand *et.al*., 2012) in their area of study.

Statistical Analysis

Table. 5 Pearson's correlation (r) values for the heavy metals Cadmium (Cd), Chromium (Cr), Nickel (Ni) and Lead (Pb)

Heavy metals	Pearsons Correlation (r) for Year	
	2013	2015
Cd and Cr	-0.999	0.680
Cd and Ni	-0.874	0.715
Cd and Pb	-0.562	0.406
Cr and Ni	0.891	0.998
Cr and Pb	0.532	-0.392
Ni and Pb	0.090	-0.347
Cu and Pb	0.767	-0.66

In the year 2010, the Pearson correlation calculated shows a very strong correlation between Cd and Pb (r = 0.991) > Ni and Pb (r = 0.979) > Cd and Ni (r = 0.979). In the year 2011 a strong correlation is seen between Cd and Pb (r = 0.998) > Ni and Pb (r = 0.916) > Cd and Ni (r = 0.890). The correlations between the heavy metals have been similar in 2010 and 2011 with slight differences in values. The correlation of Cd and Pb is higher in 2011 the correlation between Ni and Pb is higher in 2010 than 2011. The correlation in Cd and Ni is stronger in 2010 than 2011. In the year 2013 a positive correlation is observed between Cr and Ni only. In the year 2015, values of correlation are high for Cr and Ni similar to the year 2015 followed by Cd and Ni > Cd and Cr. There is an increase in the strength of correlation of Cr and Ni from 2013 to 2015.

The association between Cu and Pb in 2013 is considerably higher than the years 2004 (r = -0.304) and 2015. The year 2013 shows fewer positive correlations as observed in (Table 5). Positive correlation can also be attributed to same origin while the metals with negative correlation are an indication of distinctive sources for the metals in the river (Ahmad *et. al*., 2010).

IV. Conclusion

The present study is an attempt at assessing the heavy metals present in the downstream areas of Mithi River which probably has a visible amount of industrial activities and habitation. The values taken from sources mentioned for the year 2004, 2010 and 2011 have been compiled with the current studies which include the values from 2013 and 2015. An observation at the data, interprets the presence of heavy metals in the river. The concentrations of metals except for Lead are within the permissible limits suggested by the CPCB but none fit into the WHO limits for drinking water.

An overall view shows that the values for most of the indexes at 2013 was the lowest as compared to the other period mentioned. This could be owed to the action taken by the state government which shut a huge number of polluting industries on its banks. Additionally NEERI reported an improvement in the river water in the following year. The samples taken in 2015 again show deterioration in the quality of water. Thus, continuation of stringent laws and a combined effort by the Government and the people can help the river inch back to its original form.

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