



## **ASSESSMENT OF HEAVY METAL POLLUTION DUE TO ANTHROPOGENIC INTERVENTION IN VARIOUS RIVER PATCHES IN PUNE METROPOLIS**

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### **ABSTRACT:**

Variation in concentration of heavy metals such as Fe, Cu, Cr, Co, Pb, Cd, Ni, and Zn with pH, TDS and Electrical conductance were measured in 33 water samples collected from five different parts of Mula-Mutha river during post-monsoon 2012 in Pune urban areas, India. The waters of all river sites are neutral to slight alkaline (6.8 – 7.8). Electric conductance (EC) of the waters ranges from 514 to 863  $\mu\text{s}/\text{cm}$  and the range of total dissolved solids (TDS) is from 302 to 645 mg/l. Concentration of heavy metals were analyzed by using atomic absorption spectrometer (AAS) and the concentrations of Fe, Cu, Cr, Co, Ni, Cd, Pb and Zn in the waters range between 0.131 –2.98, 0.0006-0.11, 0–0.126, 0.00–0.0045, not detected, 0.0134–0.1, 0–0.34, 0.0057-0.378 ppm, respectively. except Ni and Zn all other heavy metals exceeded permissible limit set by WHO for drinking water 98. Geographic Information Systems, GIS 9.3 was used to Interpolate maps for spatial distribution of pH, TDS, and heavy metals in the different parts of Mula-Mutha river. Factor analysis of the heavy metals data suggest that Fe, Cu, Zn and Cd are interrelated with each other and derived significantly from the aquifer, whereas input of Pb and Co may be due to atmospheric deposition in the study area..

Anthropogenic input were found to be main sources of most of the heavy metals in the river water, However weathering of rocks and nature of the soil was the reason of behind Iron to exceed permissible limit, and decline of TDS downwardly may refer to the existence of a large amount of river Hyacinth along Mula-Mutha river.

**Keywords:** River pollution, heavy metals, Mula-Mutha river, anthropogenic intervention, water pollution.

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### **1 INTRODUCTION:**

Most of the world's drinking water supply comes from surface water resources such as lakes and rivers, and to protect public health, drinking water sources should be kept clean and free of pollution (Allan, 1995). In the recent years, specially last 25year, the rapid industrial growth, unplanned urbanization, and desire for luxuries caused the problem of river pollution to rise, particularly heavy metal pollution (Rai, 2009; Zhuang et al., 2009). In urban areas, most of the rivers are used as the end points of effluents discharged from industries, agriculture, and domestic waste( Bersinger, et al. , 2009 ). These careless disposal of these wastes contribute greatly to the poor quality of the river water (Mathuthu *et al.*, 1997).

Heavy metals released into aquatic systems are generally, bound to particulate matter, which is then incorporated into sediments (Xiangdong *et al.*, 2001). However, some of the heavy metals that are bound to the sediments may be released back to waters with a change of environmental conditions, and impose adverse effects on living organisms (Nriagu, 1989). Health related studies have reported that high intake of toxic heavy metals results in neurological and cardiovascular diseases, as well as renal dysfunction.(S.S.Dara *et al*, 2012). It

is obvious that the primary pathways of toxic metal accumulation in humans are through the intake of contaminated water and food (Akhaya et al. , 2009 ). These trace elements and their compounds can be toxic if their concentrations exceed certain limits. (Santos et al. 2004).

Pollution concentrations in river Mula-Mutha have been increased as a result of rapid urbanization and industrialization in Pune district (DDPPC, 2007). The Pavana Reveries carries both liquid effluent and solid wastes from Pimpri-Chinchwad Municipal Corporation(MSME, 2013). this industrial zone consists of various industries like pharmacies, Bajaj auto, Paper mills, Telco and lots of small industries. The Mula River is been polluted by the wastes from the western part of the city and confluence with Pavana river at Dapodi. Mutha River carries waste materials from remaining part of the city and is more polluted than the Mula River,. Thereafter, Mula and Mutha confluences at Shivajinagar near Sangam bridge.

For the present study, river water sampling was carried out from five different parts of tributaries of Mula-Mutha river in Pune city which were Pavana , Mula before joining Pavana, Mula river after joining with Pavana river but before joining with Mutha river, Mutha, and Mula-Mutha river after Sangam bridge, depending on the discharge of the patches, in such a way that 8 samples were taken from the large discharged-patches like Mula-Mutha and Mula, and the least samples were taken from Pavana patch which is the smallest patch, to assess the impact of anthropogenic activities such as agriculture, Industry, and Domestic and urban wastes released in these tributaries of Mula-Mutha river with respect to some heavy metals such as: Fe, Cu, Cr, Co, Cd, Ni, Pb, and Zn. The estimated metal levels were compared with the permissible limits laid down by World Health Organization(WHO) for acceptable drinking water quality and assess the self-purification capacity of the Mula-Mutha river.

## 2 STUDY AREA:

Pune district is located between  $17^{\circ} 54'$  and  $10^{\circ} 24'$  north latitude and  $73^{\circ} 19'$  and  $75^{\circ} 10'$  east longitude, has geographical area of 15,642 sq. km, and approximately 560 m above sea level on the Deccan plateau at the confluence of the Mula and Mutha rivers. There are three tributaries of Mula, Pavana, and Mutha that that they combine to for Mula-Mutha river.

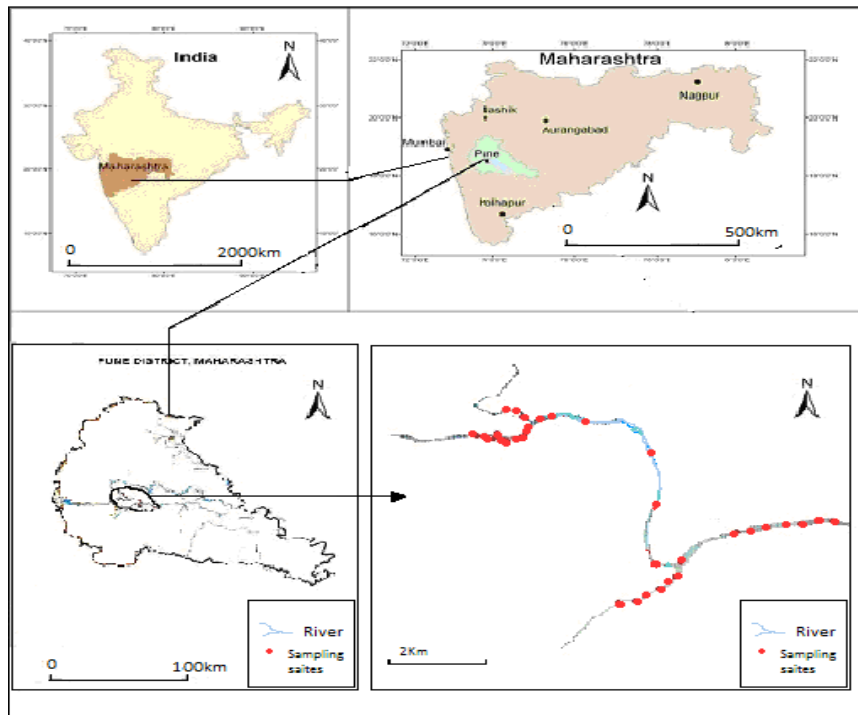


Figure. 1 Study area

### 3 MATERIALS AND METHODS

Water samples collected during post-monsoon 2012 at 33 representative sampling sites (Fig. 1) from all the five patches of Mula-Mutha river in Pune urban area which were both Pavana and Mula river before reaching Dapodi bridge, Mula river between Dapodi and Sangam bridges, Mutha river above Sangam bridge, and Mula-Mutha river after Sangam bridge.

Plastic sampling bottles were pre-conditioned with 5% nitric acid and later rinsed thoroughly with distilled de-ionized water. At each sampling site, the polyethylene sampling bottles had being rinsed before sampling was done. The collection of the samples from the river was done with hand gloved. Pre-cleaned polyethylene sampling bottles were immersed about 10 cm below the water surface in the middle parts of the river. About one liter of the water samples were taken at each sampling site. The water samples were filtered using a pre-conditioned plastic Millipore. Two sets of water samples were collected at each sampling point. One was used for in situ measurement of pH, Total dissolved solids, and Electrical conductivity. The other was acidified with 1% nitric acid solution. The acidification of the samples was to keep the metal ions in the dissolved state before measuring with AAS. The samples were kept over ice in an ice chest and transported to the laboratory. The samples were kept in a refrigerator at about 4°C until analysis was performed.

pH and EC-meter were used to measure pH, and EC, TDS was determined gravimetrically, and heavy metals were measured by using Atomic Absorption Spectrophotometer. After comparing with the WHO permissible for drinking water quality, then statistical analyses and GIS 9.3 were adopted show the highly polluted patches of the river and to identify possible sources of metal pollutants in the water, after comparing with the chemical composition of Bushe formation (Govindaraju, 1989).

### 4 RESULTS AND DISCUSSION

Table 1 shows the results of pH, TDS, electrical conductance, and amount of heavy metals for different patches of river water in Pune metropolis. Water samples were neutral to slightly alkaline (pH of 6.8–7.9), with an overall average value of 7.3. The highest value of pH was recorded at Mula patch, and the lowest pH was recorded at Mutha Batch, However no significant difference were observed in pH of the different patches. The pH of all sampling patches met the WHO Guideline (6.5–8.5) for freshwater aquatic life (WHO, 2011). Conductivity (EC) ranges from 720 to 871  $\mu\text{s}/\text{cm}$  with a mean concentration of 720  $\mu\text{s}/\text{cm}$ . The range of total dissolved solids (TDS) was from 329 to 552 mg/l. The high EC and TDS was recorded at Mula patch and reduces gradually toward downstream part.

The high concentration of both EC & TDS in the upper patches of Mula-Mutha River may be resulted from the underlying geology of the catchment area which is granitoid not limestone (Jog., (1985) ), and the weathering of granitoid leads to liberation of ions into the river. Anthropogenic activity, however, appears to be the dominant contributor of ions in the river basin. Regarding the decline in EC & TDS concentration in the downstream patches, might be due to the existence a large amount of River Hyacinths that use the dissolved solids as nutrient. The concentration of the measured heavy metals at all the 33 sampling sites were as follows: Fe(0.131-2.99)  $\pm 2\%$ , Cu(0.0006-0.1097)  $\pm 2\%$ , Cr(0-0.127)  $\pm 2\%$ , Co(0-0.004)  $\pm 2\%$ , Cd(0.106-0.013)  $\pm 2\%$ , Pb(0-0.339)  $\pm 2\%$ , Zn(0.0057-0.3782)  $\pm 2\%$ , and Ni(Nill)  $\pm 2\%$ . with an overall mean values of 0.99, 0.0416, 0.037, 0.00015, 0.0065, 0.125, 0.11 and 0 respectively. All heavy metals except Co and Ni were detected at 90% of all sampling sites, which declares a high anthropogenic intervention in the various patches of Mula-Mutha river.

This is probably due to the reality that most Co which is found in the aquatic environment is attached or combined with suspended solid particles. Also, the free cobalt in surface water bodies are absorbed by plants very rapidly (Moore, 1991). The measured heavy metals that are known as essential micro-nutrients viz. Fe, Cu, and Zn recorded their maximum concentrations at the Mutha patch, which may refer to the direct disposal of untreated sewage in this patch of Mula-Mutha river and using its bank as an open toilet by the people.

The maximum concentration of the non-essential heavy metals such as Cr, Co, Cd, and Pb in the Pavana patch, refers to the disposal of partially treated or untreated industrial waste water by the Pimpri Chinchwar Industrial area on the catchment area of the Pavana tributary. The average concentration of the measured heavy metal in all over the study area were in the order: Fe > Zn > Pb > Cd > Cu > Cr.

The Fe concentrations are high and above WHO standards at all the points. This might also be due to weathering of geological formation of under Pune metropolis that contains a high amount of Iron in its composition.

The absence of nickel in the study area might refer to its insolubility, its adsorption to sediment or soil particles and become immobile as a result, and its element accumulation in a part of various biological cycles because it is an essential micro nutrient for maintaining health in certain species of plant and animal ( Ronald Eisler 2007).

Table 1 : Table 6.3 Heavy metal analysis data of river water samples in( mg/L) except pH.

Patches	pH	TDS	EC	Fe	Cu	Cr	Co	Ni	Cd	Pb	Zn	
Mula-Mutha	1	7.2	427.5	676	0.9415	0.0006	0.0686	0	0	0.045	0.2164	0.0756
	2	7.2	425.6	673	0.6614	0.0039	0	0	0	0.04	0.1903	0.0807
	3	7.2	425.0	672	0.7527	0.0213	0	0	0	0.013	0.1922	0.0057
	4	7.2	419.2	663	0.5932	0.009	0	0	0	0.031	0.2649	0.0069
	5	7.2	428.8	678	0.8916	0.0039	0.0229	0	0	0.103	0.29	0.029
	6	7.2	416.0	658	0.8343	0.0123	0.0296	0	0	0.036	0.2463	0.0296
	7	7.1	414.7	656	0.8112	0.0239	0.0202	0	0	0.04	0.2687	0.012
	8	7.2	366.1	580	2.039	0.0387	0.0498	0	0	0.055	0.27	0.1487
Mutha	9	7.0	337.3	535	2.5871	0.0884	0	0	0	0.041	0.2948	0.2061
	10	7.0	329.0	522	1.6553	0.0497	0.0229	0	0	0.042	0.291	0.2074
	11	7.3	334.1	530	1.3033	0.0445	0.0242	0	0	0.055	0.2481	0.162
	12	7	391.7	620	2.9708	0.1097	0.0323	0	0	0.057	0	0.3681
	13	6.8	395.5	626	2.989	0.0742	0.0431	0	0	0.05	0	0.3782
	14	7	389.8	617	2.3374	0.0581	0.0296	0	0	0.05	0	0.3038
Mula+Pavana	15	7.1	483.8	764	0.7479	0.0142	0.0229	0	0	0.069	0.3041	0.0592
	16	7.0	478.7	756	0.8209	0.0148	0.0323	0	0	0.057	0	0.0624
	17	7.1	485.1	766	0.7966	0.0258	0.0377	0	0	0.062	0	0.0706
	18	7.4	464.0	733	1.0755	0.0161	0.1063	0	0	0.049	0.0187	0.1311
	19	7.4	463.4	732	1.1376	0.0232	0.0605	0	0	0.054	0	0.1456
	20	7.3	464.0	733	0.6724	0.0336	0.0659	0	0	0.061	0	0.1179
	21	7.2	470.4	743	0.7625	0.0639	0.074	0	0	0.052	0	0.1342
Pavana	22	7.5	446.7	706	1.2911	0.06	0.127	0.004	0	0.092	0.339	0.046
	23	7.5	447.4	708	0.8453	0.08	0.074	0.0015	0	0.091	0.317	0.0321
	24	7.5	444.2	702	0.9537	0.06	0.0807	0	0	0.106	0.32	0.1279
Mula	25	7.5	531.2	838	0.43	0.0426	0.0377	0	0	0.094	0	0.0769
	26	7.5	538.9	850	0.2911	0.0542	0.0121	0	0	0.088	0	0.0744
	27	7.6	545.3	860	0.296	0.0419	0.035	0	0	0.091	0	0.0655
	28	7.7	531.8	839	0.173	0.0478	0.0108	0	0	0.092	0	0.0851
	29	7.8	552.3	871	0.1851	0.0542	0.0081	0	0	0.097	0	0.0693
	30	7.9	546.6	862	0.1315	0.0503	0.0054	0	0	0.094	0	0.0737
	31	7.8	544.0	858	0.2765	0.0445	0.0417	0	0	0.09	0	0.0832
	32	7.9	549.1	866	0.2034	0.0645	0.0054	0	0	0.099	0.0224	0.0876
	33	7.2	551.0	869	0.3618	0.0458	0.0511	0	0	0.093	0.0236	0.0977
	<b>Min</b>	<b>6.8</b>	<b>329</b>	<b>522</b>	<b>0.1315</b>	<b>0.0006</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0.013</b>	<b>0</b>	<b>0.0057</b>
<b>Max</b>	<b>7.9</b>	<b>552.3</b>	<b>871</b>	<b>2.989</b>	<b>0.1097</b>	<b>0.127</b>	<b>0.004</b>	<b>0</b>	<b>0.106</b>	<b>0.339</b>	<b>0.3782</b>	
<b>Avg</b>	<b>7.3</b>	<b>455.7</b>	<b>720</b>	<b>0.99</b>	<b>0.0416</b>	<b>0.037</b>	<b>0.00015</b>	<b>0</b>	<b>0.065</b>	<b>0.125</b>	<b>0.11</b>	
<b>STdev.</b>	<b>0.3</b>	<b>67.4</b>	<b>105.3</b>	<b>0.78</b>	<b>0.03</b>	<b>0.03</b>	<b>0.001</b>	<b>0</b>	<b>0.02</b>	<b>0.131</b>	<b>0.092</b>	

Table 2 : Pearson correlation

N=33	pH	TDS	Fe	Cu	Cr	Co	Cd	Pb	Zn
pH	1								
TDS	<b>0.713</b>	1							
Fe	<b>-0.686</b>	<b>-0.765</b>	1						
Cu	0.093	-0.058	<b>0.451</b>	1					
Cr	0.015	-0.008	0.118	0.075	1				
Co	0.001	0.027	-0.064	-0.085	0.193	1			
Cd	<b>0.701</b>	<b>0.726</b>	<b>-0.465</b>	0.242	0.069	-0.050	1		
Pb	<b>-0.432</b>	<b>-0.616</b>	0.184	<b>-0.420</b>	<b>-0.358</b>	-0.165	<b>-0.455</b>	1	
Zn	<b>-0.431</b>	<b>-0.435</b>	<b>0.829</b>	<b>0.603</b>	0.062	0.030	-0.187	-0.183	1

**Significance at (0.05) , critical value =  $\pm 0.3338$**

According to Pearson correlation, A correlation coefficient (near to  $\pm 1$ ) means a good relationship between two variables, However, values between (0.33 to -0.33) means the relationship between them is neglected. Parameters having a correlation above  $\pm 0.7$  are said to be strongly correlated and highly correlated heavy metals demonstrated common source of pollution (Romic M, Romic D, 2002).

For the present study:

\*An almost high positive correlations between (Fe with Zn, TDS with Cd, and Cu with Zn) and the a positive correlation between( Fe with Cu and Zn with both Cr and Cu) reports that these parameters more or less have a common source of pollution.

\* The high negative correlations between (pH with Fe, and TDS with Fe and Pb) and negative correlation between ( pH with Pb and Zn, TDS with Zn, Fe with Cd, and Pb with pH, TDS, Cu, Cr, and Cd) may be due to local man-made activities.

**Interpolation maps for spatial distribution of pH, TDS, and heavy metals**

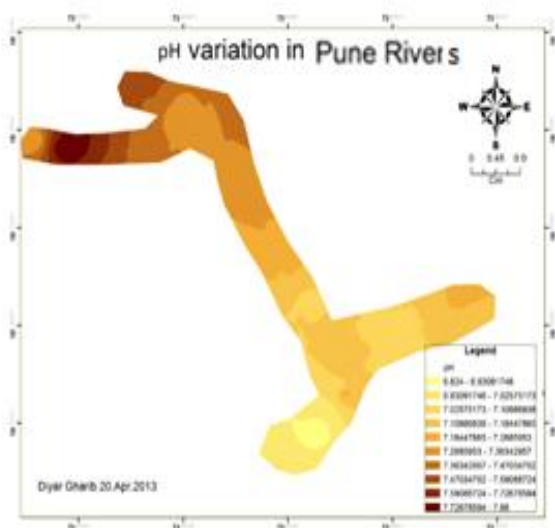


Figure2. pH variation in Mula-Mutha patches

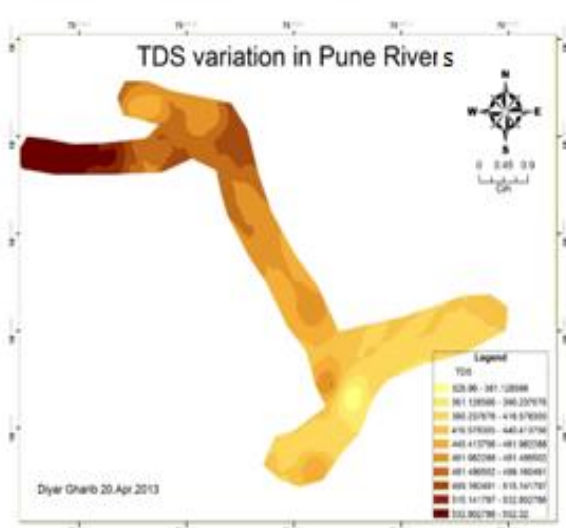


Figure3. TDS variation in Mula-Mutha patches

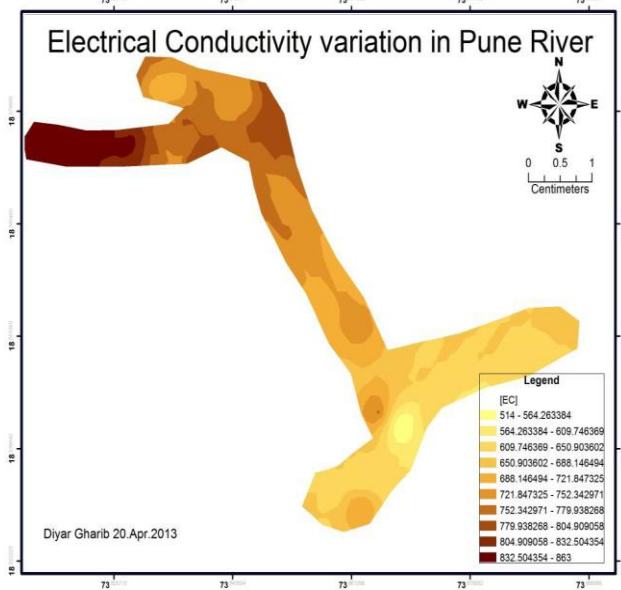


Figure4. EC variation in Mula-Mutha patches

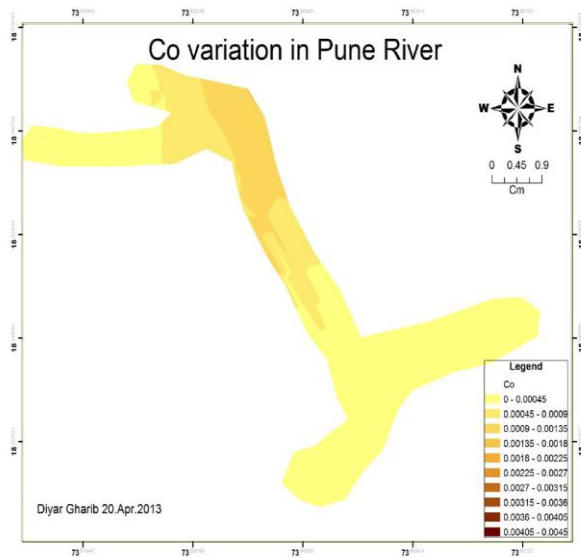


Figure 5. Co variation in Mula-Mutha patches

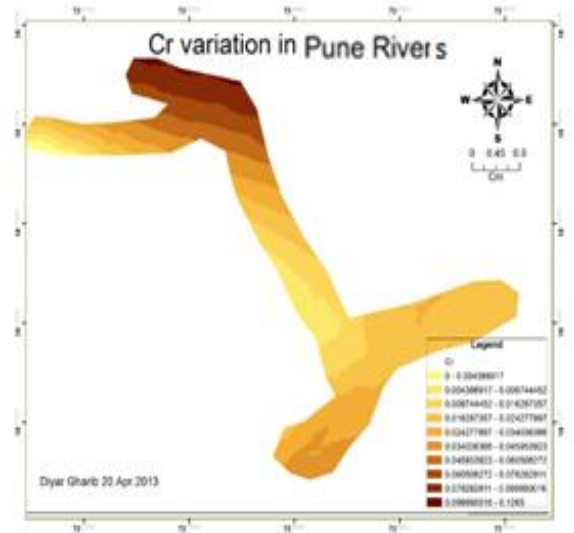


Figure 6. Cr variation in Mula-Mutha patches

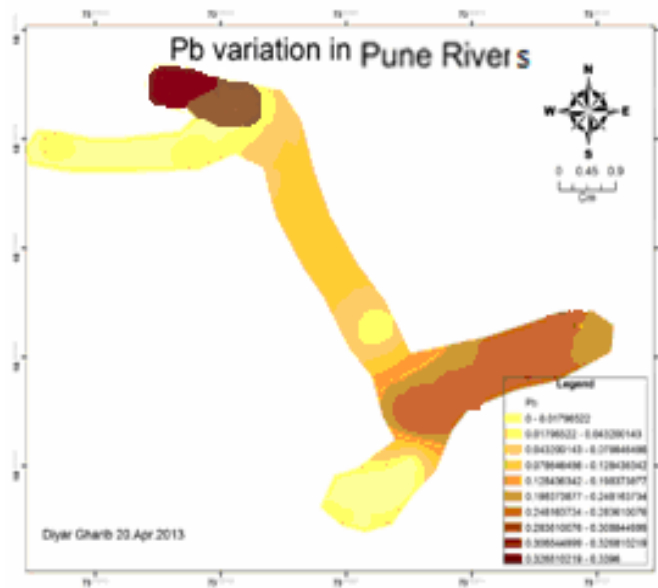


Figure 7. Pb variation in Mula-Mutha patches

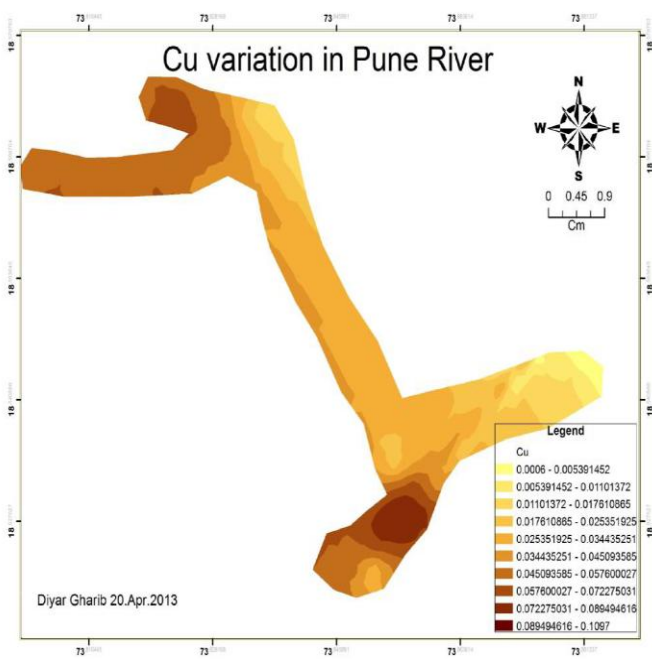


Figure 8. Cu variation in Mula-Mutha patches

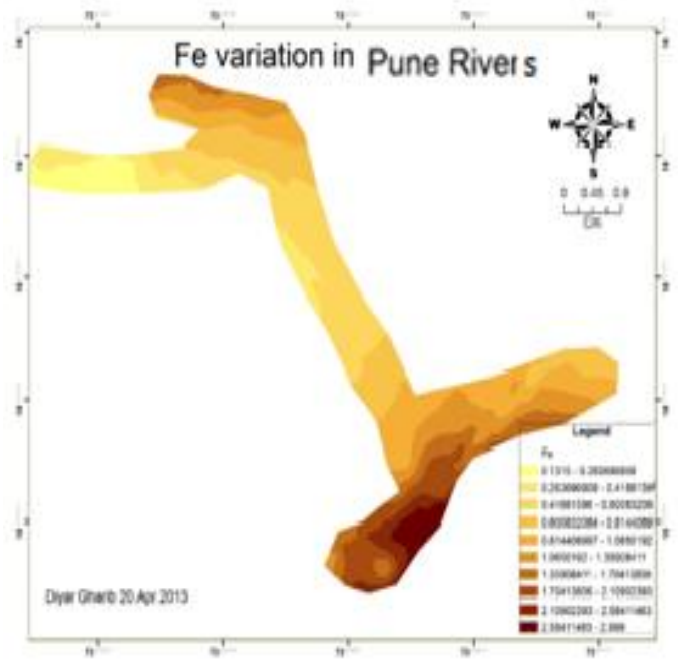
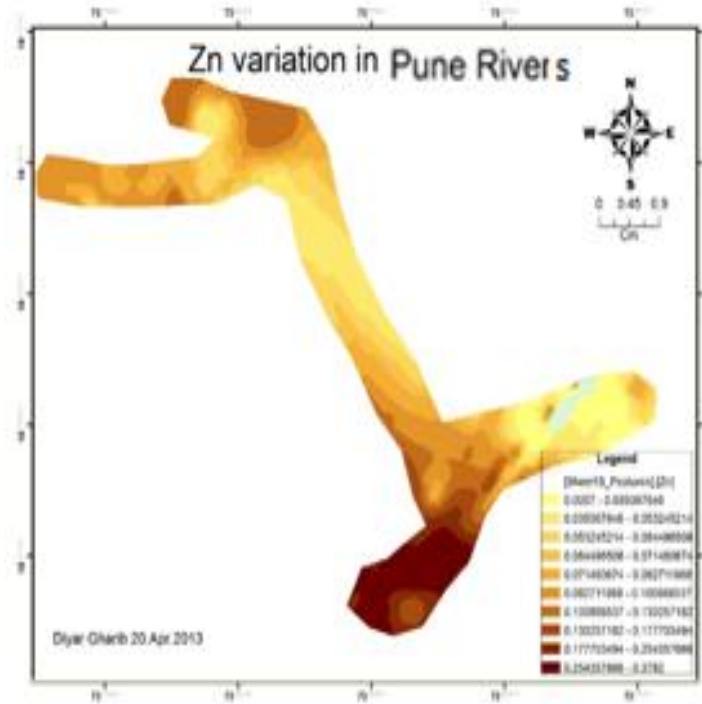


Figure 9. Fe variation in Mula-Mutha patches





**Figure 10. Zn variation in Mula-Mutha patche**

GIG 9.3 is used to illustrate the spatial distribution of the pH, TDS, and some heavy metal concentrations shown in the above figures, in such away that the darkest colored regions have the highest concentration of that parameter.

For the present study:

- \* Fig. 2 and 3 illustrates that the high concentration of both EC & TDS recorded at the upper patches of Mula-Mutha River.
- \* Fig. 4, 5, and 6 illustrates that the maximum concentration of the non-essential heavy metals such as Cr, Co, Cd, and Pb in the Pavana patch.
- \* Fig. 7, 8, and 9 illustrates that the highest concentrations of Cu, Fe, and Zn recorded at Mutha patch.

## CONCLUSIONS:

The study shows that the concentration of TDS and EC decline as the river passes through Pune city, which is due to the existence of a large amount of water Hyacinth found in the rivers especially during post monsoon season.

The Iron levels of river water in all sampling site are above permissible limits which refers to the nature of the geological formation and the soil present in the area .

The most dominant heavy metal in the rivers is Cadmium, which is 30 times more than the permissible limit in upper patch of the river. due to improper effluents of the Pimpri Chinchwad industrial area.

The absence of nickel in the study area might refer to its insolubility, its adsorption to sediment or soil particles and become immobile as a result, and its element accumulation in a

part of various biological cycles because it is an essential micro nutrient for maintaining health in certain species of plant and animal.

The absence of Cobalt in the surface river environments may be due to that cobalt is needed by blue-green algae (Cyanobacteria) and other nitrogen fixing organisms.

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