



## Determination of Trace Elements with respect to its Suitability for Drinking and Irrigation in Hub Dam, Pakistan

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### Abstract:

*The present study documents seasonal variations with respect to concentrations of selected trace metals such as chromium, iron, nickel, copper, zinc, cadmium, lead, mercury and arsenic at Hub Dam, Sindh, Pakistan, during 2012. We assessed dam water suitability for domestic and irrigation purpose and their impacts on water quality. The result demonstrates that concentration of trace metals is slightly higher than WHO standards and NEQS for drinking purpose except zinc. The obtained results were also compared with NEQS standards for irrigation. Among the metals analyzed Cr, Cu and Cd values were exceeding the defined limit. The Hub dam reservoir exhibited the average concentration of trace metal Cr = 0.09, Fe = 0.72, Ni = 0.07, Cu = 2.52, Zn = 1.11, Cd = 0.11, Pb = 0.17, Hg = 0.01 mg l<sup>-1</sup> while the arsenic (As) concentration was below deductible limit during the study period. It is concluded that Hub Dam water is chemically unsafe and unfit to some extent for human consumption, irrigation and for the growth of aquatic flora until its proper treatment.*

**Key words:** Asebot, Afromontane forest, degradation, reforestation programme

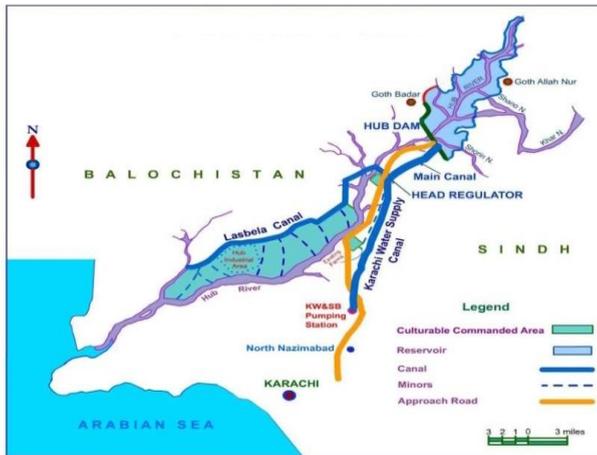
### Introduction

Water is nature's most wonderful, abundant, useful compound, a fundamental necessity for life. Without proper functioning water supply, it is difficult to imagine productive human activity, be agriculture or forestry, livestock, farming or fisheries, trade or industry (Tatawat and Singh Chandel 2007). Wetlands are a significant factor in the health and existence of other natural resources of the state, such inland lakes, ground water, fisheries and wildlife (Akbar et al., 2009). Pakistan, despite having an arid climate, supports over 780,000 ha of wetlands, covering 9.7% of the total land area, with 225 nationally significant wetlands, of which 19 have been recognized as Ramsar sites of global significance (Chaudhry 2010, 49).

Pakistan has three categories of protected areas: National Parks, Wildlife Sanctuaries, and Game Reserves (Khan et al. 2010). The KPAC comprises Hub Dam as a Wildlife Sanctuary (Khan et al. 2013). Change in water quality caused by pollution can adversely affect wetlands, causing a loss in biodiversity and productivity (Chaudhry, 2010).

The fate and effects of pollutants discharged into a particular water body will depend not only on the amount of polluting substances emitted but also on the hydrological, physical, chemical and biological conditions characterizing the water body (Nazif, Perveen, and Shah 2006). Nazif, Perveen, and Shah (2006) suggested that water pollution by heavy metals is mainly caused by point source emissions from mining activities and a wide variety of industries, while non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead, arsenic and antimony (Kennish 1992).

Hub Dam (25° 15'N 67° 07'E) was constructed on Hub River in 1981, at a distance of 56 km North of Karachi in Sindh - Balochistan province border (Fig. 1) (Ghalib, Hasnain, and Khursheed 2000).



**Fig. 1. The water canal system of Hub Dam**

Main Dam is 15,640 meters long, of which 10,240 m lies in Sindh, while the rest in Balochistan (Khan et al. 2012). The dam is situated in an area of semi-aridity and desert with sedimentary rocks, with a few small islands in the midst of the reservoir. The Hub River separates the provinces Balochistan and Sindh, each of which receives water by a canal from the Hub Dam reservoir (Qaimkhani et al. 2005). The water level in the reservoir fluctuates widely according to rainfall in the water catchment area, which extends over 3410 sq. miles. The topography of the upper catchment is sub – mountainous to hilly and plain. The area is generally barren with sparse vegetation at certain locations. The catchment of the Hub reservoir is wholly rain fed. The dam is relatively shallow with maximum depth of 9.6 m. The water has relatively high concentration of dissolved salts of sulphates, sodium and chloride and dissolved oxygen which results into high greater primary and secondary production (Ghalib, Hasnain, and Khursheed 2000).

The climate of the area is predominantly arid and with an average annual rainfall of less than 200 millimeters (mm). The temperature often exceeds 36 Celsius (°C) during summer (Ghalib, Hasnain, and Khursheed 2000).

The Hub Dam Canal system consists of the Main Canal, Karachi Water Supply Canal, Lasbella Canal and the Bund Murad Minor. The water level in the dam depends on the

amount of rainfall in the water catchment area. There has been no ample rain for the previous five years and the water level in the reservoir has decreased significantly, posing a problem for the drinking water supply to Karachi west.

## **Objective**

The objective of the present study is to assess the seasonal variations with respect to trace metals of Hub Dam and its suitability for domestic and irrigation purposes along with analysis of the environmental impact.

## **Materials and Methods**

During the study period, the main dam (N 25° 14' 35.5, E 67° 06' 45.8) was selected as a study site, most of the samples were collected in 1000 ml polyethylene screw – cap bottles in order to obtain the water of the required depth. A very crucial step in analyzing the samples was the transformation of a sample into an analytic solution. For the preparation of reagents, Analytical Grade (AR) chemicals were used for the determination of water quality parameters and standard analytical methods were carried out.

To give aqueous phase, the acidified water samples were treated with reagent and trace metal was analyzed by Flame Atomic Absorption (Mastoi, Khahawar, and Bozdar 1997). By gravimetric methods TDS and Conductivity were measured by light and dark bottles method (Welch 1952). PH was recorded with Orion 420 pH meter. Digested liquid wastes were used to analyze Cr by Graphite Furnace method, Fe by Flame Atomic Absorption Spectrophotometer, Ni by Graphite Furnace method, Cu and Zn by Flame Atomic Absorption Spectrophotometer, As by Hydrate Generation method, Cd and Pb by Graphite Furnace method. The instrument (Perkin Elmer Model No. A analysts 700) used different techniques, such Flame atomic absorption spectrometer, Graphite and hydrates system to analyze the chemicals. Determination for each metal was taken out in triplicate for getting representative results.

## **Results and discussion**

The water of the reservoir was found to be clear, odorless and tasteless. Selected trace metals were chromium, iron, nickel, copper, zinc, cadmium, lead, mercury and arsenic. In addition, physical parameters such as TDS, conductivity and pH were also recorded. The results were compared with WHO and NEQS Standards for drinking and irrigation.

It is expected that in the study area these metals get into aquatic environment from anthropogenic sources and distributed in water, suspended solids and sediments from the course of their transportation (Olajre and Imeokparia 2000). Except few metals, most of these metals show a higher value as per defined limit of WHO (World Health Organization) and NEQS (National Environmental Quality Standard) for drinking and irrigation standards.

Seasonal analysis is carried out to identify the variability of these metals during the year. The collected data was grouped into seasons, summer (March-June), monsoon (July-October) and winter (November-February). The data shows lower concentration of these metals during the monsoon period, this being the result of dilution factor due to heavy rainfall from August to September. The maximum concentration was recorded during summer, the result of evaporation, except for Arsenic during the study period. Data suggested that concentration of these metals in hub dam reservoir was the result of anthropogenic influence due to discharge of sewerage, human waste and human activities.

The concentration of physical parameters and trace metals in the Hub reservoir are shown in Table 1 and in Table 2 where the minimum, maximum, mean, and standard deviation are listed with the comparison of standards for drinking and irrigation purpose.

Parameters	min	max	mean	sd	NEQS for drinking	WHO St	NEQS for Irrigation
<b>TDS</b>							
summer	483	612	537	54.851	1000	1000	1000
monsoon	484	500	492	8	1000	1000	1000
winter	487	510	497.25	9.639	1000	1000	1000
<b>pH</b>							
summer	6.8	7.1	6.925	0.125	6.5-8.5	6.5-8.5	6.5-8.4
monsoon	7.1	7.3	7.2	0.1	6.5-8.5	6.5-8.5	6.5-8.4
winter	7.1	7.4	7.275	0.125	6.5-8.5	6.5-8.5	6.5-8.4
<b>Conduc tivity</b>							
summer	495	598	550.5	55.764	-	-	1.5
monsoon	480	515	501.666	18.929	-	-	1.5
winter	568	600	586.5	13.478	-	-	1.5

**Table 1. Changes TDS, pH and EC of Hub Dam water**

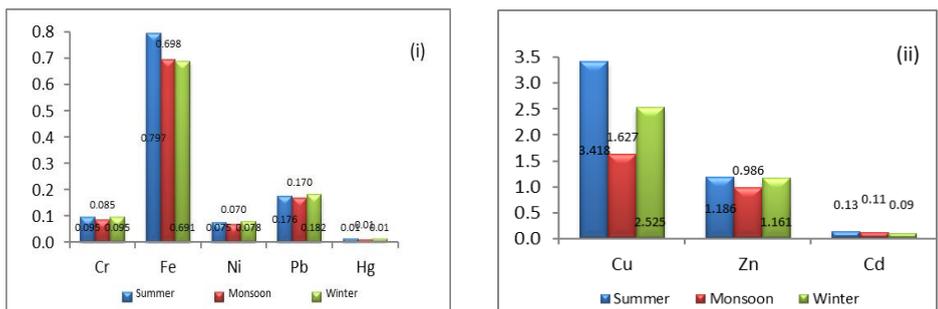
Metals	Min	Max	Mean	Standard Deviation	NEQS For Drinking	WHO Standard	NEQS For Irrigation
<b>Chromium</b>							
summer	0.09	0.1	0.095	0.005	0.05	0.05	0.01
monsoon	0.06	0.1	0.08	0.02	0.05	0.05	0.01
winter	0.09	0.1	0.095	0.005	0.05	0.05	0.01
<b>Iron</b>							
summer	0.324	1.324	0.797	0.450	0.3	0.3	5
monsoon	0.451	0.895	0.623	0.238	0.3	0.3	5
winter	0.543	0.789	0.690	0.112	0.3	0.3	5
<b>Nickel</b>							
summer	0.061	0.081	0.075	0.009	0.02	0.02	0.2
monsoon	0.051	0.077	0.066	0.013	0.02	0.02	0.2
winter	0.07	0.08	0.077	0.005	0.02	0.02	0.2
<b>Copper</b>							
summer	2.632	4.512	3.418	0.796	2	2	0.02
monsoon	0.944	1.666	1.285	0.362	2	2	0.02
winter	2.214	3.22	2.525	0.472	2	2	0.02
<b>Zinc</b>							
summer	0.781	1.621	1.186	0.364	5.0	3	2
monsoon	0.521	1	0.831	0.268	5.0	3	2
winter	0.971	1.332	1.161	0.155	5.0	3	2
<b>Cadmium</b>							
summer	0.072	0.192	0.129	0.049	0.01	0.003	0.01
monsoon	0.092	0.132	0.108	0.020	0.01	0.003	0.01
winter	0.014	0.149	0.066	0.068	0.01	0.003	0.01
<b>Lead</b>							
summer	0.162	0.184	0.175	0.010	0.05	0.01	0.1
monsoon	0.161	0.175	0.167	0.007	0.05	0.01	0.1
winter	0.175	0.195	0.182	0.008	0.05	0.01	0.1
<b>Mercury</b>							
summer	0.012	0.015	0.013	0.001	0.001	0.001	0.01
monsoon	0.01	0.012	0.011	0.001	0.001	0.001	0.01
winter	0.01	0.014	0.012	0.001	0.001	0.001	0.01
<b>Arsenic</b>							
summer	ND	ND	ND	ND	0.05	0.01	0.1
monsoon	ND	ND	ND	ND	0.05	0.01	0.1
winter	ND	ND	ND	ND	0.05	0.01	0.1

**Table 2. Average concentrations of trace metals comparing with WHO, NEQS for drinking and irrigation ND: Not detected**

The Hub Dam water exhibited an alkaline pH in the range of 6.8-7.4, with an average of 7.1. Seasonal variability reveals that the lowest pH was observed during monsoon. The result, however, was within the prescribed limit of WHO and NEQS for drinking and irrigation water. TDS results demonstrate that Hub Dam reservoir is within the safe limit of WHO and NEQS for drinking and agriculture production. The seasonal variability trend of conductivity is also observed in summer, monsoon and winter. Significant seasonal changes were also observed with respect to conductivity as the trend which was recorded in other parameters. The lowest conductivity was observed during monsoon. Results of conductivity are in safe limit and have not shown any adverse effects on human consumption and irrigation.

Cr is a widely distributed metal in earth's crust. Seasonal observation of Cr was recorded. Nazif, Perveen, and Shah (2006) concluded that heavy metal contents of canal water decrease as it approaches its end and this might be due to sedimentation. In all seasons Cr is shown to be slightly exceeding as compared to prescribed limits of WHO and NEQS standards for drinking water i.e. 0.05 mg-l, while NEQS for irrigation is 0.01 mg-l (Table 2). Fig. 3 (i) demonstrates the seasonal variations with different standards that reveal that Cr is slightly exceeding. Khan et al. (2012) reported the higher value as compared to the set limit of WHO Standard.

■ NEQS for drinking purpose      ■ WHO Standard for drinking  
■ NEQS for irrigation purpose



**Fig. 3 (i & ii) Variation in the concentration of trace metals**

Fe is the most abundant metal found in the natural water body, within the range of 0.5 – 50 mg-l (WHO, 1993). WHO and NEQS Standard for this metal is 0.3 mg-l. Data of this study shows that the estimated value slightly exceeds the WHO and NEQS Standards for drinking water. This study, with reference to the Fe level, does not point to any significant adverse effect on biodiversity as it is within acceptable limits. This is because of the presence of microorganisms in the reservoir which convert ferrous into ferric hydroxide by taking dissolved iron as an energy source (Trivedi 1993). On this basis, it can be assumed that the concentration of Fe in the reservoir could be attributed to human activities such as discharge of untreated sewage. Fig.3 (i) shows the monthly Fe concentration with respect to different standards for drinking and irrigation. The obtained results of Fe in all seasons is within the limit and the water is suitable for irrigation with respect to irrigation standard of NEQS i.e. 5.0 mg-l. Reemtsma, Gnriss, and Jekel (2000) reported a high concentration of Fe content in urban runoff provided by municipal waste water.

Nickel is normally found in the water body by the infiltration of sewage water. The WHO Guideline and NEQS value for drinking and irrigation is 0.02 mg-l and results are found within the prescribed limits. Fig.3 (i) portrays the monthly concentration of Ni as related to different standards.

The level of copper demonstrates a higher value with respect to WHO and NEQS Standard, i.e. 2.0 mg-l, and for irrigation the described value - i.e., 0.2 mg-l. The observed value for this study is within the acceptable limits having no adverse effect on aquatic biodiversity. It can be used for drinking and irrigation purposes after treatment. Fig. 3, ii shows the concentration of Cu - its value is higher during the year particularly in the month of June (summer). Ahumada et al. (1999) concluded that untreated wastewater increases Cu content in the soil.

Recorded value of Zn demonstrates an acceptable range in all seasons and it did not exceed the WHO and NEQS limit that is 3.0 mg-l for drinking and 2.0 mg-l for irrigation. The monthly graph reveals that all the recorded values of Zn are

within the prescribed limit, so the water of Hub dam water is safe both for drinking and for irrigation supplies (Fig.3, ii).

The concentration of Cd was also recorded during different seasons. Cadmium toxicity affects kidney, heart and liver (Mench, Baize, and Mocquot 1997). Even if in a low concentration, Cd has adverse effects both on human and aquatic life. In the present study, the documented observed value of Cd in all seasons was slightly higher than the WHO Standard i.e. 0.003 mg-l for drinking and slightly higher than the prescribed limit of NEQS i.e., 0.01 for both drinking and irrigation. The lowest concentration was recorded during the monsoon, which was the result of rainfall followed by high river discharge from upstream environment. Setia et al. (1998) concluded that sewage water contains 4 - 10 times more Cd content than tube well water. Boruvka et al. (1996) reported that a high concentration of Cd content in floodwater increases its concentration in the contaminated soils. The result of Cd shows that this can affect aquatic biodiversity and human health. It is obligatory to supply water for domestic and irrigation usage only after treatment in order to protect human health.

Pb is a normally toxic and cumulative poisonous metal present in the water body. In the present study, Pb value was significantly higher than the prescribed value of WHO Standard i.e. 0.01 mg-l and NEQS standard i.e 0.05 mg-l for drinking. As to the irrigation quality of Hub dam water, the obtained values are little exceeding the prescribed value of NEQS i.e., 0.01 mg-l. Fig. 3(i) demonstrates that during the summer season, especially in May and June, the values are increased due to raise in temperature and decreased in the rainy period due to dilution.

Mercury is not normally found in the water body but it could be found as a result of discharge of sewage effluent in the reservoir. The WHO Guideline and NEQS value for drinking is 0.001 mg-l and for irrigation purpose 0.01 mg-l. The present observed value of mercury was not exceeding much these prescribed limits. The documented result reveals that the Hub dam water, with respect to Hg, is safe both for drinking and

irrigation. Fig. 3(i) portrays the monthly concentration of Hg with the different standards value.

Arsenic is a highly toxic metal and it affects the digestion tract, abdominal cavity and muscle tissue in fish, but in the present investigation no traces of arsenic were observed in any season in the Hub dam reservoir.

Based on bar diagram indicated plots it could be concluded that during summer the recorded concentration is higher comparatively to monsoon and winter. The seasonal correlation among the physico-chemical parameters (TDS, EC and pH) and trace metals of the Hub Dam water was studied and the results are shown in Table 3 (i-iii).

	TDS	EC	pH	Cr	Fe	Ni	Cu	Zn	Cd	Pb	Hg
TDS	1.000										
EC	0.701	1.000									
pH	0.294	-0.390	1.000								
Cr	-0.078	0.521	-0.426	1.000							
Fe	0.058	0.713	-0.620	0.948	1.000						
Ni	-0.087	0.387	-0.191	0.966	0.840	1.000					
Cu	0.878	0.954	-0.165	0.282	0.481	0.179	1.000				
Zn	0.679	0.980	-0.484	0.401	0.641	0.231	0.943	1.000			
Cd	-0.001	0.663	-0.608	0.966	0.997	0.868	0.421	0.584	1.000		
Pb	0.255	0.865	-0.776	0.697	0.889	0.503	0.687	0.873	0.857	1.000	
Hg	-0.078	0.521	-0.426	1.000	0.948	0.966	0.282	0.401	0.966	0.697	1.000

**Table 3. (ii). Correlation of TDS, EC, pH and different trace metals during monsoon**

	TDS	EC	pH	Cr	Fe	Ni	Cu	Zn	Cd	Pb	Hg
TDS	1.000										
EC	0.656	1.000									
pH	0.199	0.246	1.000								
Cr	-0.150	0.600	-0.229	1.000							
Fe	0.320	0.882	-0.115	0.889	1.000						
Ni	-0.882	-0.223	-0.132	0.577	0.146	1.000					
Cu	-0.775	-0.962	-0.058	-0.507	-0.846	0.395	1.000				
Zn	0.499	0.515	-0.666	0.447	0.650	-0.299	-0.698	1.000			
Cd	-0.914	-0.361	0.115	0.337	-0.096	0.946	0.569	-0.591	1.000		
Pb	0.376	0.832	0.685	0.481	0.645	0.019	-0.658	-0.042	0.032	1.000	
Hg	0.704	0.992	0.349	0.507	0.817	-0.293	-0.947	0.438	-0.394	0.862	1.000

**Table 3. (iii). Correlation of TDS, EC, pH and different trace metals during winter**

During the present investigation in summer highly significant positive correlation is observed as to the trace metal concentration between Cr to EC (0.994) and Cu to Cd (0.984) and during monsoon a highly positive correlation was found between Cr and Hg (1.000), while in winter – between EC and Hg (0.992) and between Ni and Cd (0.946). It therefore suggests

that these metals are moving together during the monitoring period.

The mean concentrations of the metals were recorded in the following order:  $Cu > Zn > Fe > Pb > Cd > Cr > Ni > Hg$  during the present investigation. Reemtsma, Gnirss, and Jekel (2000) reported that Fe, Pb and Zn originate in the urban runoff, while Cr and most alkaline earth metals are provided by the municipal wastewater. Canal sediment could act as sink for a wide range of contaminants including heavy metals from various sources (e.g. Agriculture and wastewater discharge) (Stephens et al. 2001). Kar et al. (2008) reported that excess of heavy metal load in water is due to discharge of industrial effluents and municipal waste, geology of reservoir bed and catchment area.

## **Conclusion**

The present investigation indicates that there is no significant excessive concentration of heavy metals recorded at sampling sites except in few places where a negligible amount of toxicity was documented. Based on chemical examination, reservoir water is fit for drinking and irrigation purposes in the case of substances other than copper, cadmium, lead and mercury. The excessive heavy metal load of water can be attributed to the discharge of sewerage, human waste, the geology of Hub Dam bed and catchment area. Near the adjoining area of the study, there are some agriculture lands the margins of which may also add trace metal contamination in the long run and affect the water quality of the reservoir. Adoption of adequate measures to remove the trace metal load and renovation of sewage treatment plants are suggested to avoid further deterioration of the Hub Dam water quality.

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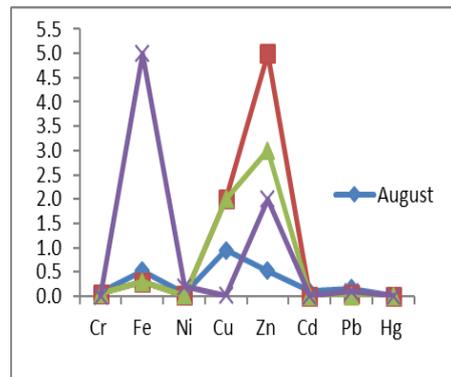
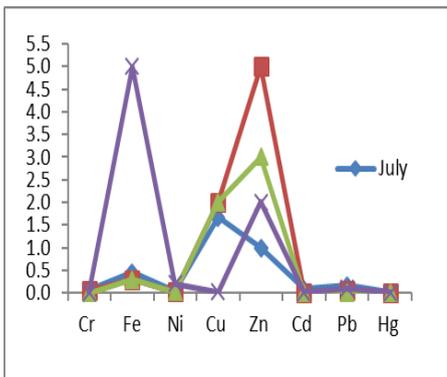
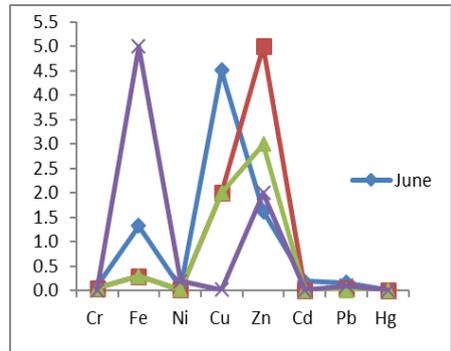
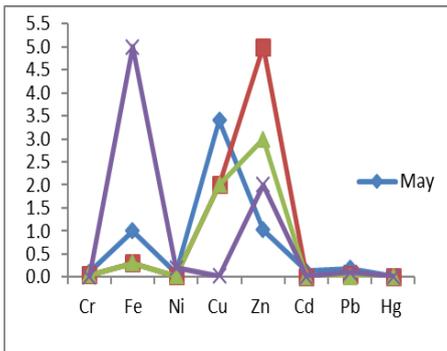
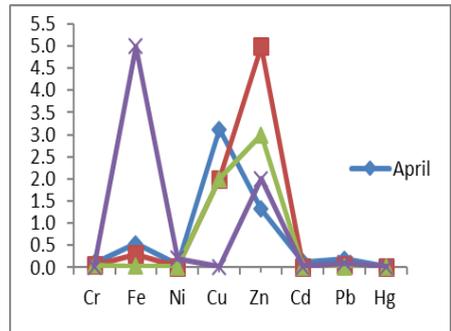
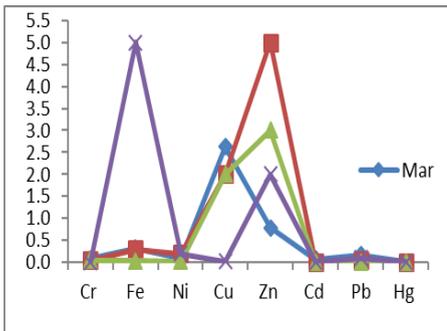
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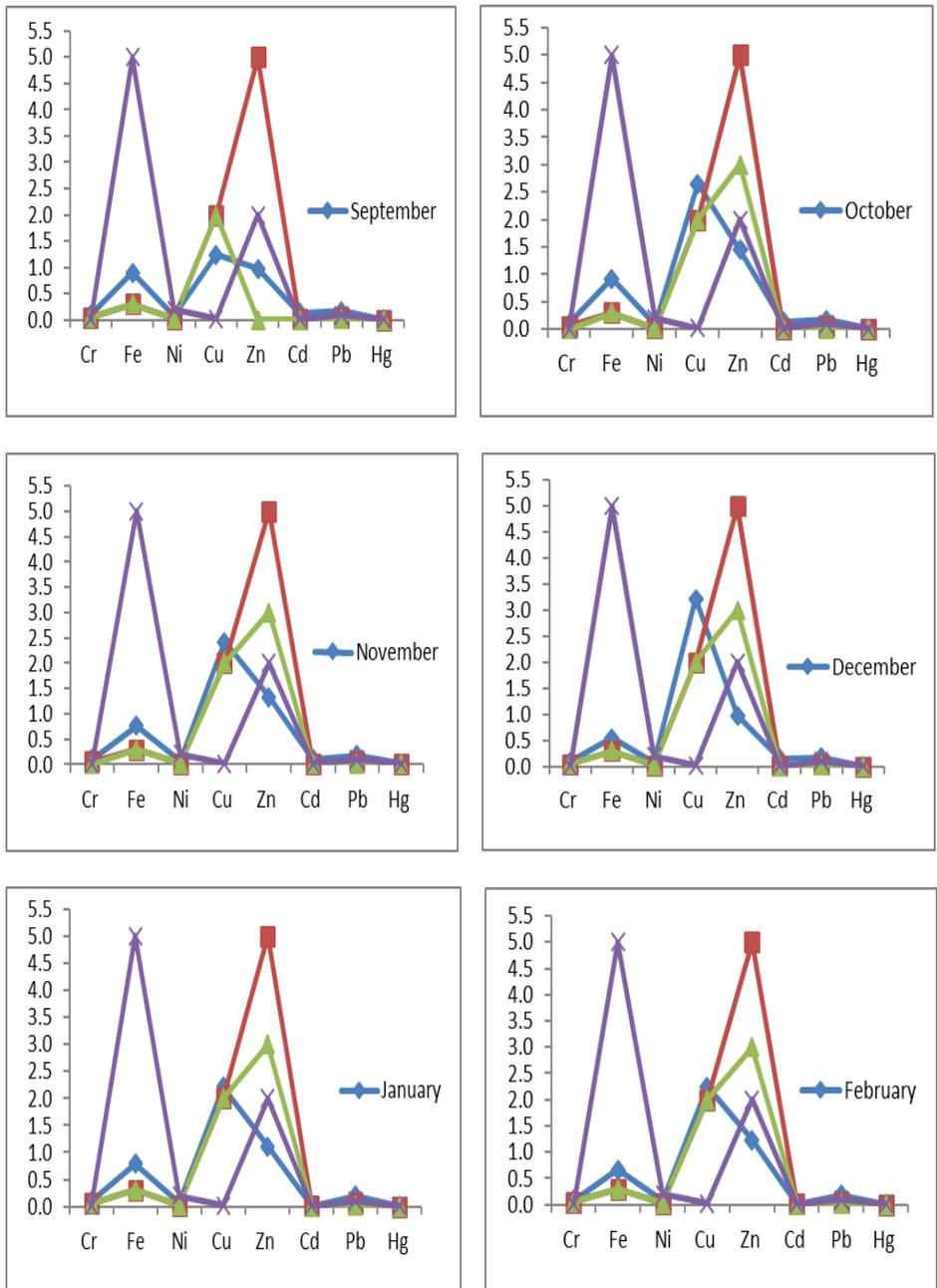
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**Annex 1**





**Fig.2. Graphs showing the month wise comparison of trace metals with their different standards.**