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Evaluation of Water Quality Pollution Indices for Heavy Metal Contamination Monitoring in the Water of Harike Wetland (Ramsar Site), India

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Abstract- The diverse functions of wetlands are being adversely affected by human activities. Harike wetland has high ecological significance as it provides home to diverse flora and fauna, habitat for feeding and breeding and social interactions. This paper discusses an integrated approach of pollution indices and statistical techniques to assess the intensity of heavy metal pollution discharged from various industries in Harike wetland. This wetland is highly polluted due to the rapid industrialization, urbanization and dumping of solid wastes. The water quality of the wetland has been studied with reference to various toxic metals. The metals analyzed include lead, chromium, iron, copper, nickel, zinc and cadmium. The quality of water has drastically deteriorated due to the mixing of the heavy metals. Most of the metal ions were in higher concentration compared to the international standards. It has been observed that the quality of water is not safe for various aquatic and even unfit for human drinking and irrigation purposes, therefore, necessary conservation and management measures should be taken to improve the deteriorating water quality of this globally recognized wetland.

Index Terms- Harike wetland; Ramsar site; Heavy metals; Pollution; Water quality

I. Introduction

From the very dawn of human civilization, due to uncontrolled greed, the over utilization of natural resources has been taken place which caused unparallel devastation. Recently, with the unplanned growth of industrialization, rapid urbanization and degradation of aquatic resources, by using them as dumping grounds for sewage, deforestation, depletion of water resources has played a crucial role in deterioration of aquatic ecosystems on the earth. Wetlands are more affected these days because they receives polluted water from various sources through rivers and streams. Wetlands support unique aquatic biodiversity which is facing a serious threat. Some of the important organisms came under threatened categories of IUCN. Heavy metals, including both essential and non-essential elements, have a particular significance in eco-toxicology. They are highly persistent and have the potential to be toxic to the living organisms. Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring their concentration in water (Ebrahimpour and Mushrifah, 2008). Human activities have led to accumulation of toxic metals in the natural environment (Karbassi and Bayati, 2005) and the extensive exploitation of natural resources has led to increased pressure on aquatic ecosystems. Resultantly, due to an increased load of heavy metals the aquatic ecosystems have severely disrupted. Elevated concentrations of pollutants in these systems have resulted in bioaccumulation of toxic metals and a serious environmental problem, which threatens aquatic organisms and human health (Sasmaz et al., 2008).

Many large industrial factories including cement factories, paint manufacturing plants, dying industries, pesticide and insecticides factories, leather industries and tanneries are located along the banks of the river Sutlej and discharges polluted water into it and this water ultimately reaches at Harike wetland. Effluents from these factories have caused severe contamination of water in this wetland. The purpose of this study was to determine the concentrations of lead (Pb), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), cadmium (Cd), aluminum (Al) and iron (Fe) in water of Harike wetland. The data collected will be shared with the Stake holder agencies to start immediate pollution mitigation and conservation measures.

II. MATERIALS AND METHODS

Study Area

The study area is situated in three districts of Punjab state i.e. Kapurthala, Tran Taran and Ferozepur with 4100ha area (Figure.1). This wetland included into the list of Ramsar sites in 1990. Harike wetland located at latitude of 31.17° N and longitude of 75.20° E. This wetland is also important because situated on the confluence of two rivers of the Indus river system i.e. Beas and Sutlej. The journey of the river Beas ends here and the river Sutlej flows downstream and enters into Pakistan. This is a riverine wetland, but due to large area it supports different type of habitats like palustrine, lacustrine and swamps. Due to its diverse nature, it supports vast variety of valuable flora and fauna. Unfortunately, this important aquatic ecosystem receives large quantity of untreated industrial effluents from adjoining cities through the inflow Rivers which are posing a serious threat to its existence.

Water Sampling

Water samples were collected from March, 2013 to February, 2014 in four different seasons of the year from five sites in Harike wetland. The surface water samples were thoroughly filtered through cellulose nitrate filter paper to eliminate suspended solids and stored in plastic bottles with one liter capacity. 1 ml of concentrated nitric acid was added to it for preservation. Heavy metal analysis has been done using Atomic Absorption Spectrophotometer (AAS).

Figure 1. Map of Harike wetland.

Pollution evaluation indices

Generally, pollution indices are applied to estimate the pollution of the water samples under consideration. The indices used in this study, are heavy metal pollution index (HPI), heavy metal evaluation index (HEI) and degree of contamination (C_d). These indices are used to evaluate quality water for drinking as well as irrigation purposes. The HPI and HEI methods provide an overall quality of the water with regard to heavy metals.

Heavy metal pollution index (HPI)

HPI index was developed by assigning a rating or weightage (W_i) for each chosen parameter. The rating system is an arbitrarily value between 0 to 1 and its selection depends upon the importance of individual quality considerations or it can be defined as inversely proportional to the standard permissible value (Reddy, 1995; Mohan et al. 1996). In computing the HPI for the present water quality data, the concentration limits i.e. the standard permissible value (S_i) and highest desirable value (I_i) for each parameter were taken from the WHO standards.

The HPI is determined by using the expression below (Mohan et al. 1996):

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi}$$

Where Q_i is the sub-index of the ith parameter. W_i is the unit weightage of the ith parameter and n is the number of parameters considered. The sub-index (Q_i) is calculated by

$$Q_i = \sum_{i=1}^{n} \frac{\{Mi(-)Ii\}}{(Si-Ii)} \times 100$$

Where *Mi*, *Ii* and *Si* are the monitored value of heavy metal, ideal and standard values of the ith parameter, respectively. The sign (-) indicates numerical differences of the two values, ignoring the algebraic sign.

Heavy metal evaluation index (HEI)

The HEI method gives an overall quality of the water with respect to heavy metals (Edet and Offiong, 2002) and is computed as:

$$HEI = \sum_{i=1}^{n} H_c / H_{mac}$$

Where H_c is the monitored value of the ith parameter and H_{mac} the maximum admissible concentration of the ith parameter.

Degree of contamination (C_d)

The contamination index (C_d) sumarises the combined effects of several quality parameters considered harmful to domestic water (Backman et al. 1997) and the contamination index is calculated from equation below:

$$C_d = \sum_{i=1}^{n} C_{fi}$$

Where

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$$

Where C_{fi}, C_{Ai} and C_{Ni} represent contamination factor, analytical value and upper permissible concentration of the ith component, respectively (N denotes the 'normative value').

Statistical analysis

To identify the relationship between various heavy metals in the water samples statistical analysis has been done by using Pearson's correlation matrix with the help of SPSS software.

III. RESULTS

Heavy metal pollution is a serious and widespread environmental problem due to persistent toxicity, non biodegradable and bio-accumulation properties of these contaminants. The mean values of heavy metals detected in water from Harike wetland are presented in Table 1 and are compared to the WHO maximum permissible limits. Most of the heavy metals are above permissible limits prescribed under WHO standards.

Heavy Metals in Water

Lead

The level of Pb is 0.53 ppm which is above permissible limits in water comes from various industries like paint industry, refining and manufacturing of Pb coating goods. It is very toxic in nature and causes many diseases. A remedy must be sought for the gradual phasing out of Pb from various industries by using new technologies.

Copper

The Cu content in water is 0.26 ppm considered above permissible limit. The source of copper is mining, metal production, storage batteries and fertilizer production industries. Aquatic organisms are potentially at risk from Cu exposures, mitigation measures are required to reduce Cu inflow into the wetland.

Cadmium

The average Cd content in water is 0.01 ppm. Cadmium is non-essential element. The source of Cd in water is electroplating, alkaline batteries, mining and plastic industries. It interferes with metabolic processes in plants and can bioaccumulate in aquatic organisms and enters in food chain (Adriano, 2001). The concentration obtained during present course of work is above permissible limits.

Chromium

The average concentration of Cr in water is reported to be 0.12 ppm. This is possibly due to release of Cr in the effluent during various industrial operations. The effluents with high Cr content should be treated before discharge.

Nickel

The concentration of Ni is reported as 0.01ppm. Nickel can be toxic to aquatic organisms such as reduction in skeletal calcification and diffusion capacity of gills (Moore, 1991). The source industries are electroplating, steel industries, ceramics, storage batteries, dying and colouring of glass.

Zinc

The average concentration of Zn in water is 0.69 ppm which is below permissible limit. Zinc is used in plastic industries, cosmetics, steel processing, printing ink and in rubber production.

Manganese

The average abundance of manganese is 0.02 ppm which is below permissible limit. It is used in metallurgical processes, manufacturing of dry cell batteries and fertilizers.

Cobalt

The concentration of cobalt is 0.007 ppm which is within the acceptable range. Cobalt is present in industrial effluent coming from chemical industries, electrical and electronics and auto part manufacturing.

Correlation matrix analysis

In the present study, the correlation coefficient among various heavy metals has been calculated. The statistical analysis (Table 2) showed both positive and negative correlation among different metals. It is clear from the results that copper was positive correlated with most of the other metals whereas lead (Pb) is negatively correlated with other metals. Cadmium and Chromium is highly correlated with each other.

Pollution indices

The heavy metal pollution index of all the heavy metal have been calculated individually using the standards Table 3 and is represented by HPI, with range 115.4-7000 and mean concentration value 1304.65 of all metals, including all the seasons. The components considered include Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The results of pollution evaluation indices are presented in Table 4. The result of indices showed that the HPI for all the metals were above the critical limit of 100 proposed for drinking water by Prasad and Bose, 2001.

The degree of contamination (C_d) was used as reference to estimate the extent of metal pollution (Al-Ami et al. 1987). C_d may be grouped into three categories as follows: low ($C_d < 1$), medium (C_d = 1-3) and high ($C_d > 3$). The range and mean values of C_d were 0.4-352.33 and 44.85. The value of contamination index exceed 3, suggesting that water is highly polluted.

The heavy metal evaluation index used for a better understanding of pollution indices. The mean value of HEI was 45.85. By following the approach of Edet and Offiong (2002), the proposed HEI criteria for the samples are as follows: low (HEI $<$ 10), medium (HEI = 10-20) and high (HEI $>$ 20). The present level of HEI shows that the water quality falls within high zone of pollution.

IV. DISCUSSION

Metals are reported to be well concentrated in the water (Simpson, 1982; Everall et al., 1989). Bioaccumulation of these metals in many fish species and their organs have been reported world widely by Kumada et al., 1980; Wasternhagen et al., 1980; Osborne et al., 1981; Norris and Lake, 1984 and Evans, 1987. These metals in trace amount may play important role in the biochemical life process of the aquatic organisms (Tay et al., 2009). However, their high concentration becomes lethal to fish and other aquatic organisms when the duration of exposure to these metals is prolonged (Deekay et al., 2010). Harike wetland also receives heavy metals pollution from various sources which persists through out the year. As, observed during present investigation the level of some highly toxic metals is above permissible limits. The high concentration is posing a big threat to valuable flora and fauna existing there.

Elmaci et al., 2007 reported that in water samples of Lake Uluabat Zn and Cu concentrations were significantly higher due to the industrial and domestic discharge. The same observations are found in inland waters of Hong Kong (Zhou et al., 1998). Panday et al., 2010 observed that in Ganga river, more than 80% of the water samples Cd and Ni levels above the recommended maximum permissible concentration, the kind of results was reported in Ona river by Adefemi and Awokumi, 2010. Similar observations are found in present study, concentration of Cd and Ni is above the maximum permissible concentration recommended by WHO.

Khan et al., 2005 states that some elevated concentration of heavy metals (Pb, Cr, Hg, Cd, Fe, Cu, Ni, Zn) were recorded in the surface water bodies near NLC corporation due to the untreated wastewater discharge, fly ash ponds and industrial effluents from the Neyveli mines industrial complex. Davis et al., 2006 and Abdulah, 2007 stated that high concentration of heavy metals present in the sediments than the water, because sediments accumulate more heavy metals. Glenn et al., 2009 observed the presence of heavy metals in the coastal lagoon of manila bay are due to the direct deposition of these metals from air pollution.

Thus, the present study is an attempt to detect the heavy metal concentration in the water of Harike wetland. If this trend is allowed to continue unabated, it is most likely that the food web complexes in this wetland might be at the highest risk of induced heavy metal contamination. This alarming concentration may also escort discomfort to the people living in the vicinity of this wetland. Hence, strict management actions should be taken into consideration in order to protect the ecological sustainability of this wetland.

V. CONCLUSION

The study shows that the water of Harike wetland exhibits high concentration of heavy metals like Cd, Cu, Pb, Cr, Ni, Co and Fe. The contamination index C_d (>3) place water quality in high contamination level and heavy metal pollution index HPI on the other hand consider the level of contamination critical. Fluctuations in concentration of various heavy metals have been observed in different seasons. The correlation coefficient indicates positive and negative correlation of these metals with each other. The revelations during the present study are startling and summons immediate attention from the stake holder agencies for its conservation management and sustainable development so that optimum utilization of this wetland may be carried out.

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Table 1. Heavy metal analysis of surface water of Harike wetland

Site	Season	Copper (Cu)	Iron (Fe)	Lead (Pb)	Cadmium (Cd)	Zinc (Zn)	Nickel (Ni)	Chromium (Cr)	Manganese (Mn)	Beryllium (Be)	Cobalt (Co)
Harike wetland	**Winter**	0.283	2.231	0.536	0.026	1.003	-	0.042	-	0.054	0.021
	Spring	0.10	0.032	0.7021	0.034	-	-	0.251	-	-	0.0067
	Summer	0.5435	1.895	-	-	0.907	0.042	0.217	0.086	-	-
	Autumn	0.116	1.067	0.907	0.011	0.872	0.0289	-	0.0319	0.239	-
Mean±S.D.		0.26±0.20	1.30±0.98	0.53±0.38	0.01±0.01	0.69±0.46	0.01±0.02	0.12±0.12	0.02±0.04	0.07±0.11	0.0021±0.067
WHO Permissible Limits (mg/l)		0.02	1	0.05	0.005	1	0.02	0.05	0.05	-	-

Table 2. Correlation matrix among different heavy metals in surface water of Harike wetland

	Copper	**Iron**	**Lead**	**Cadmium**	**Zinc**	**Nickel**	**Chromium**	**Manganese**	**Beryllium**	**Cobalt**
Copper	1									
Iron	0.70424	1								
Lead	-0.96668	-0.53932	1							
Cadmium	-0.68919	-0.49035	0.54835	1						
Zinc	0.52997	0.91237	-0.30033	-0.64405	1					
Nickel	0.58924	0.28634	-0.47913	-0.97532	0.47187	1				
Chromium	0.2851	-0.41707	-0.51357	0.10069	-0.66139	0.0093644	1			
Manganese	0.78644	0.36039	-0.72542	-0.94171	0.41907	0.94922	0.23868	1		
Beryllium	-0.47614	-0.021724	0.67051	-0.2259	0.37008	0.23813	-0.8256	-0.073327	1	
Cobalt	-0.099122	0.37376	0.095811	0.62507	0.12961	-0.78142	-0.26087	-0.6775	-0.26574	1

Table 3. Standard used for the indices computation.

	W	**S**	**I**	**MAC**
Cu	0.001	1000	2000	1000
Fe	0.005	300	200	200
Pb	0.7	100	10	1.5
Cd	0.3	5	3	3
Zn	0.0002	5000	3000	5000
Ni	0.05	20	20	20
Cr	0.02	50	50	50
Mn	0.02	100	500	50

W weightage (1/MAC)
S Standard permissible in ppb
I Highest permissible in ppb
MAC Maximum admissible concentration/upper permissible (Adapted from Siegel, 2002)

Table 4. Evaluation indices.

Parameter	C_d	HPI	HEI
Cu	0.74	174	0.26
Fe	5.5	1100	6.5
Pb	352.33	577.77	353.33
Cd	2.33	350	3.33
Zn	0.862	115.5	0.13
Ni	0.5	1000	0.5
Cr	1.4	7000	2.4
Mn	0.6	120	0.4
Maximum	0.5	7000	353.33
Minimum	352.33	115.5	0.4
Mean	44.85	1304.65	45.85