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Heavy Metal Pollution Monitoring of Yamuna from Dak Patthar to Agra

Rahat Zehra*, Madhulika Singh[1], Jyoti Verma[2]

[*]Research Scholar, Amity University, Amity Institute of Geo Informatics and Remote Sensing, , Noida, Uttar Pradesh - 201313, India.
ORCID I'd:- 0000-0002-2042-050X.

[1]Advisor, Amity University, Amity Institute of Geo Informatics and Remote Sensing, Noida, Uttar Pradesh - 201313, India.

[2]Assistant Professor, University of Allahabad, Prayagraj, Uttar Pradesh- 211002, India. ORCID I'd:- 0000-0002-0503-5996.

Abstract

With 14 sampling sites between Dak Patthar to Agra, first time an attempt is made to evaluate the heavy metals viz. Iron, Copper, Zinc, and Manganese in the Yamuna using Indices; Heavy Metal Pollution Index (HPI); Heavy Metal Evaluation Index (HEI), Contamination index (Cd), Principal Component Analysis (PCA), and Cluster analysis (CA).The average concentrations in parts per billion in the increasing order were Cu (292.7)> Fe (309.23) > Mn (475.15) >Zn (3643.9). Resultant average values of HPI 551.40, HEI 12.07, Cd 8.07 with Principal Component1's eigenvalue 55.49 and 2 clusters of sites based on metal concentration were obtained.

Keywords- Heavy Metal Pollution Index (HPI), Heavy Metal Evaluation Index (HEI), Contamination Factor (C_d), Cluster analysis (CA), Principal Component Analysis (PCA).

INTRODUCTION

Originating at Yamnotri glacier the Yamuna; along with its tributaries Tons, Betwa, Chambal, Ken, and Sindh contribute to 70.9% of the catchment area and balance 29.1% is direct drainage of the main river as reported by the Central Water Commission in 2007. Yamuna catchment basin area shares 40.2% of the Ganga river basin and in total 10.7% of the country. The average annual rainfall along the river

stretch varies from 65 to 125 cm, with the river's annual flow and usage of 10,000 cubic billion meters and 4400 m3/s, respectively (Keshari, 2011).Lots of studies in the literature have focused on heavy metal pollution of water resources all around the world (Nabi bidhendi *et al.,* 2007; Wang *et al.,* 2007; Zhang *et al.,* 2009; Nasrabadi *et al.,* 2010b). The water quality monitoring of River Yamuna has indicated a significant presence of several heavy metals in its water (Rawat *et al*., 2003; CPCB, 2006; Jain, 2009; Kaur & Mehra, 2012; Malik *et al*., 2014). Table1.gives the Concentration of Heavy Metals in various river systems of the Indian subcontinent.

Table1: Concentration of Heavy Metals in various river systems of Indian subcontinent.

River	Cr	Cd	Pb	Mn	Fe	Co	Ni	Cu	Zn	References
Gandak	19.86	0.716	15.1	- - -	- - -	13.66	13.91	15.37	41.315	Singh et al, 2018
Gandaki	3.02	0.02	0.61	6.63	- - -	0.55	1.41	1.89	127.7	Pant et al, 2019
Ganga	0.013	0.009	0.04	- - -	- - -	- - -	- - -	0.019	0.072	Gupta et al, 2008
Ganga	0.189	0.004	- - -	- - -	1.652	0.334	0.00286	- - -	- - -	Sharma et al, 2018
Ganga	- - -	0.032	0.02	- - -	- - -	- - -	0.045	0.031	0.444	Singh et al,2018
Ganga	261	5	555	- - -	- - -	- - -	- - -	158	- - -	Kumar et al, 2019
Ganga	2.792	0.007	0.02	- - -	0.627	- - -	- - -	0.007	- - -	Ahmad et al, 2019
Ganga	37	2.92	166.62	335.69	8074	3.4	238.7	256.36	213	Singh et al,2020
Ghaghara	0.007	0.043	0.01	- - -	- - -	0.027	0.018	0.032	0.031	Singh et al,2016
Gomati	- - -	- - -	0.32	0.11	1.179	- - -	- - -	0.016	0.168	Trivedi et al, 2016
Gomati	0.005	N.D	0.039	0.0053	0.117	- - -	0.017	N.D	0.032	Singh et al,2005
Kali	0.09	0.08	0.19	- - -	1.77	- - -	- - -	- - -	29.71	Mishra et al, 2015
Kali	0.087	0.024	0.34	0.04	- - -	- - -	- - -	- - -	0.079	Malik et al, 2015
Kosi	123.0	0.59	36.1	- - -	- - -	19.59	52.65	43.63	93.36	Li et al , 2019
Kosi	1.091	0.051	0.01	- - -	- - -	- - -	- - -	- - -	- - -	Idrees et al, 2020
Ramganaga	- - -	0.0129	0.0096	1.3091	5.2178	- - -	- - -	- - -	0.1058	Khan et al, 2017

Son	0.007	0.086	0.02	- - -	0.62	- - -	- - -	- - -	0.15	Ahirwar et al, 2015
Yamuna	0.008	- - -	- - -	0.136	0.421	0.00064	0.018092	0.001898	0.003467	Kaur et al, 2012
Yamuna	147.1	47.6	116.4	- - -	10,488	- - -	375.5	2151.8	1500.7	Bhardwaj et al, 2017
Yamuna	0.035	0.037	0.02	- - -	6.467	- - -	0.0254	0.081	1.3651	Yadav et al,2019
Yamuna	0.513	0.715	1.09	- - -	- - -	- - -	- - -	- - -	0.948	Ghosh et al, 2019
Brahmaputra	0.01	0.001	0.11	1.44	- - -	0.2	0.44	0.12	0.01	Bhuyan et al, 2019
Cauvery	0.32	- - -	9.95	1.25	- - -	2.23	5.25	1.12	10.7	Begum et al, 2009
Godavari	10.12	0.99	4.11	- - -	0.18	- - -	17.29	42.8	0.094	Hussain et al, 2017
Kameng	N.A	0.069	0.375	0.23	0.769	- - -	- - -	0.083	0.036	Sharma et al, 2018
Mahanadi and Brahmani	N.A	- - -	- - -	1500	8000	- - -	- - -	126	272	Mishra et al,2014
Mithi	455	223	755	231	- - -	- - -	607	- - -	- - -	Singare et al, 2012
Subarnarekha	0.9	- - -	- - -	12	133.8	0.6	25.2	16.6	3.1	Giri et al, 2013
Swarna	N.A	0.17	1.48	- - -	- - -	- - -	- - -	4.74	9.25	Kalra et al, 2019
Yamuna	- - -	- - -	- - -	**0.4751**	**0.3092**	- - -	- - -	**0.3230**	**3.6439**	**Present study**

*concentration in ppm.

The integration of Heavy Metal Pollution Index (HPI); Heavy Metal Evaluation Index (HEI), Contamination index (Cd), Principal Component Analysis (PCA), and Cluster analysis (CA) (Swanson *et al*. 2001; Arora and Mehra 2009; Vieira *et al*. 2012; Mohan *et al*. 1996; Edet and Offiong 2002; Prasad and Mondal 2008) provides detailed, quick, and reliable information for decision-makers to adopt or implement strategies related to water pollution and scarcity (Rawat & Singh, 2018).

STUDY AREA

The study area lies between the Dak Patthar (30.502487 N, 77.798393 E) to Agra (27.205341N, 78.036348E) covers polluted areas of the sacred river with the belt of luxuriant alluvial soil and densely inhabited area. The study area and sampling points in parts of the River Yamuna from Dak Patthar to Agra are displayed in Fig1 and Table2 gives the description of 14 sampling sites.

Table 2: Description of 14 sampling sites of river Yamuna from Dak Patthar to Agra.

Site Code	Site Name	Geographical Coordinates	Distance From Sampling locations (km)	Description
1	Dak Patthar	30.502487 N, 77.798393 E	Start point	Pristine condition of river, small fishes/ organisms, ingenious change in terrain profile observed.
2	Paonta Sahib	30.433365N, 77.620863 E	23	Remnants of devout offerings, settlements disposing waste into river
3	Kalanour	30.069167N, 77.351698 E	79	NHAI 4 lane road network under construction ,Metallurgical industries, Thermal plant fly ash pond, SAIL plant, cremation site
4	Cullackpur	28.858605N, 77.209396 E	175	Water turns dark brown; stingy odour, cattails, flowering rush and bulrushes. Stonewort, plankton algae, Water Hyacinth, mosses, Myriophyllum (milfoil)
5	Sonia Vihar	28.721756N, 77.241404 E	29	Delhi Jal Board Plant, Entry point of river into Delhi
6	Najafgarh Drain	28.706072N, 77.231996 E	7.7	Confluence of river with Najafgarh drain (the major polluting drain), Signature bridge constructional waste dump on site, dark black water , extreme odour
7	Delhi Old Bridge	28.661981N, 77.252145 E	7.7	Densely populated, largest concentration of small scale industries
8	Yamuna Bank	28.615742N, 77.255569 E	9	Drain of IP Power plant, blackish color. stingy odour
9	Sarae Kale Khan	28.596835N, 77.268218E	8.2	Weed plants were found in large number, stingy odour with inorganic waste.
10	Okhla Bird Sanctuary	28.535793N, 77.328382E	14	Confluence of Shahdara drain (2^{nd} major polluting drain) with Yamuna, cow shed, direct release of untreated waste.
11	Kaliya Ghat	27.582988N, 77.687496E	144	Brown color water, untreated waste outlets,
12	Gokul Barrage	27.439817N, 77.717803E	29	Water color turns green, algal growth, bathing and open defecation.
13	Poiya Ghat	27.254229N, 78.022088E	67	Stingy odour, agricultural activities and dumps of waste.
14	Rambagh	27.205341N, 78.036348E	8	Cremation site, water slightly clear in brown color, no fishes or organism; exit point of Agra.

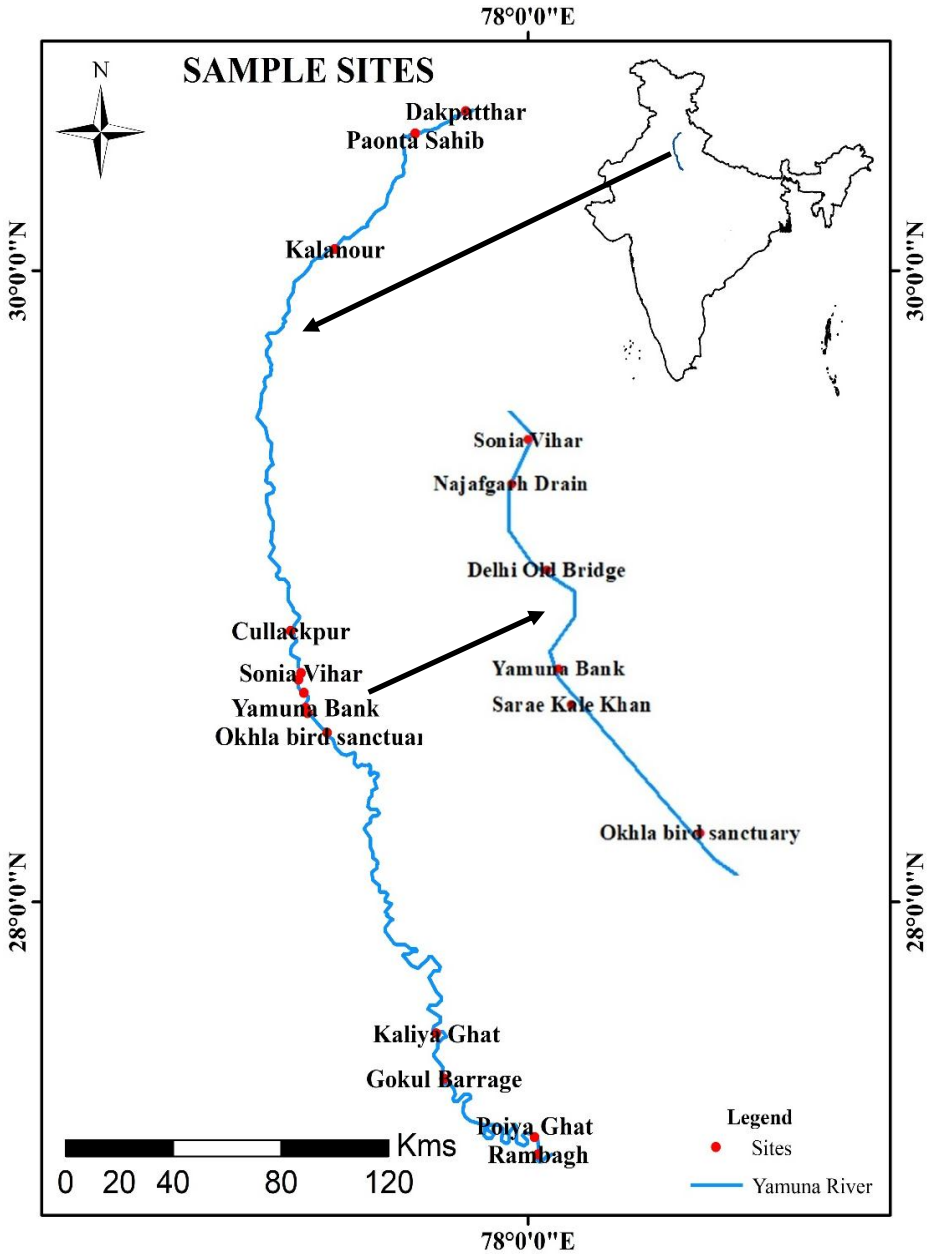

Fig.1 Location map of the study area and sampling points in parts of the River Yamuna from Dak Patthar to Agra.

MATERIAL AND METHODS

The water samples were collected from the river with evident point sources of pollution in the satellite imageries and concentrations of anthropogenic activities. Two sets of sterilized High-Density Polyethylene Bottle (HDPE) with a capacity of 500ml each were filled from a 20cm river water depth. The coordinates of the sites were taken with Garmin eTrex 10 Global Positioning System. In-situ parameters (pH,

Temperature, Total Dissolved Solids, Electric Conductivity, Dissolved Oxygen, Turbidity) were measured using a Horiba Multi-parameter probe. The samples preserved at 4°C after acidifying with concentrated Nitric Acid were transferred to the laboratory for further analysis as per the standard procedure. NovAA350-Analytikjena Atomic Absorption Spectrophotometer (AAS) was used for Heavy Metal detection of Iron, Zinc, Manganese, and Copper and an average of three replicates were recorded.

For calculating Heavy Metal Pollution Index (HPI) values; Eq.1. (Mohan *et al* 1996; Ichwana, *et al*. 2016) weighted arithmetic averages of the concentrations were used

$$\mathbf{HPI}=\sum_{i=1}^{n} WiQi/\sum_{i=1}^{n} Wi \qquad (1)$$

Wherein, Wi is the unit weightage defined as the reciprocal value of Si which is the maximum permissible limit for irrigation purposes of water as per FAO (Ayers and Westcot, 1994). The number of parameters n and Qi being the sub-index of the ith parameter are calculated as in Eq.2. Further, Mi has monitored values of the heavy metal and Si the standard value for the i-th parameter. Both these values are in ppm.

$$Qi=\sum_{n=1}^{n} \frac{Mi}{Si} * 100 \qquad (2)$$

Further Heavy Metal Evaluation Index (HEI) is used to obtain the overall quality of water concerning the heavy metal concentrations measured.

$$HEI = \sum_{i=0}^{n} Hc/Hmac$$

Where in; Hc and Hmac are the monitored value and maximum admissible concentration (mac) of the ith parameter (Pundir *et al*., 2018). Table 3 was used for the calculation of the HPI and HEI.

Table 3: Heavy Metals Permissible Concentration by World agencies and Standard values for the indices computation.

Heavy Metals	US EPA, 2008	WHO 2008	EU 1998	BIS (ISO: 10500) 2012	ICMR1975	CPCB 2012	W	S	I	MAC
	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)	(µg/l)				
Fe	300	NGL*	200	300	300	300	0.005	300	200	200
Zn	5000	NGL**	NM	5000	5000	5000	0.0002	5000	3000	5000
Mn	50	400	50	100	100	2000	0.02	100	500	50
Cu	1300	2000	2000	50	50	3000	0.001	1000	2000	1000

W Weightage (1/MAC) (adopted from Edet and Offiong 2002),S standard permissible in ppb, I highest permissible in ppb, MAC maximum admissible concentration/upper permissible.

NM- Not Mentioned; NGL No Guideline, because it is not of health concern at concentrations normally observed in drinking water, but may affect the acceptability of water at concentration above 300 µg/L ; NGL** No Guideline, because it occurs in drinking-water at concentrations well below those at which toxic effects may occur; USEPA- United States Environment Protection Agency; WHO- World Health Organization; EU- European Standards; BIS- Bureau of Indian Standards; ICMR- Indian Council of Medical Research; CPCB- Central Pollution Control Board.*

Source: Kaur & Mehra, 2012; Saha & Paul, 2016

Contamination index (Cd) as Backman *et al* 1997 demonstrated analyzes the cumulative effect of various parameters on the quality of water for domestic purposes. This index is the sum of contamination factors of the individual parameters beyond their permissible standard values as represented in Eqn. below.

$$Cd = \sum_{i=1}^{n} Cfi$$

Where *Cfi = CAi/ CNi – 1.*

The Cfi, CAi, and CNi represent the contamination factor, analytical value, and upper permissible concentration, respectively, of the ith component. N denotes the 'normative value'; values for CNi were taken as MACs given in Table 3.

Principal component analysis (PCA) interprets the variance of large datasets without losing their dimensionalities using the Eigenvalue and Eigenvectors of the original variable. PCA is one of the best multivariate statistical techniques for extracting linear relationships among a set of variables (Simeonov *et al* 2003).

Cluster Analysis (CA- hierarchical clustering); primary objective is to identify relatively homogenous groups or clusters of objects based on their similarities/dissimilarities (Wai *et al* 2010). In the clustering procedure z-transformation of the raw data was performed with squared Euclidean distance as a similarity measure and Ward's method of the linkage.

RESULTS AND DISCUSSION

The onsite observations were noted and described in Table2. The results derived are summarized in Table 4; with average concentrations of the heavy metals; total metal load at the sites and the physical parameters measured namely pH, Temperature, and Total Dissolved Solids. The pH values range 6.91-7.86 with the average temperature being 20.7 ° C. The average Total Dissolved Solids (TDS) was 468.21 ppm with a maximum of 885ppm at Najafgarh Drain site and a minimum of 79 at Dak Patthar site. The average concentrations in parts per billion of the metals were in the increasing order Cu> Fe>Mn>Zn; with values 292.7> 309.23> 475.15> 3643.9. The maximums were Copper 892.2 ppb (site12), Iron 754.7 ppb (site 3), Manganese 982.2 ppb(Site 10) while Zinc 8146.9ppb (site 9). Concerning Total Metal Load; Sarae kale khan site was most contaminated with 9303.9 ppb. However, the average value of Metal Load was 4720.99 ppb.

Table 4: Site wise Physical and Heavy Metal Concentration load of River Yamuna.

Site No.	Location	pH	Temp (°C)	TDS (ppm)	Copper (in ppb)	Iron (in ppb)	Manganese (in ppb)	Zinc (in ppb)	Metal Load (ppb)
1	Dak Patthar	7.86	19.8	79	25.5	67.7	217	1014.3	1324.5
2	Paonta Sahib	7.3	19.7	175	3.1	219.1	262	1101.4	1585.6
3	Kalanour	7.44	21	184	324.7	388.4	119.2	1648.2	2480.5
4	Cullackpur	7.53	21	247	84.9	754.7	123.5	1624.1	2587.2
5	Sonia Vihar	7.21	20.5	312	47.2	289.1	261.8	3137	3735.1
6	Najafgarh Drain	6.91	19.8	885	195.9	267.1	321.5	3178.9	3963.4
7	Delhi Old Bridge	7.2	19.8	559	820.3	393.8	775.7	3168.5	5158.3
8	Yamuna Bank	6.98	21.7	614	253.7	313.5	778.1	7189.7	8535
9	Sarae Kale Khan	7.49	19.8	633	120.8	219.5	816.7	8146.9	9303.9
10	Okhla Bird Sanctuary	7.45	19.2	586	146.7	183.4	982.2	2977.4	4289.7
11	Kaliya Ghat	7.51	21.1	526	111.6	197.1	949.5	6257.4	7515.6
12	Gokul Barrage	7.38	24	528	892.2	364.2	920.5	1597.7	3774.6
13	Poiya Ghat	7.55	21	679	783.9	283.1	48.9	6038.7	7154.6
14	Rambagh	7.16	21.7	548	287.3	388.6	75.6	3934.4	4685.9

The Site wise results of the three indices: HPI; HEI; Cd for the study area are compiled in Table 5. The mean values of the indices are HPI as 551.4; HEI as 12.07 and Cd as 8.07. Further, the correlation of the three indices with metal concentrations being studied to a significant level of >0.5 was noted in Table 6. A highly positive correlation of Manganese with the three indices was observed. Iron showed a negative correlation with the indices. PCA with Loading values >0.3 were considered. It was observed from Table 7 that PC1 having eigenvalue as 55.49 had a maximum variance of 98.85 %. The other two PC2 and PC3 had 0.76 % and 0.38% of the variance. Cluster Analysis cophenetic correlation coefficient was noted to be 0.7776. Fig2 shows the 14 sites divided into two clusters according to the metal concentrations. The average value of water quality parameters for each cluster is listed in Table 8.

Table 5: Sitewise Results of the three indices (HPI; HEI; C_d) for the study area.

S.No	HPI	HEI	C_d
1	188.74	4.91	0.91
2	286.98	6.56	2.56
3	175.84	4.98	0.98
4	261.19	6.65	2.65
5	314.71	7.36	3.36
6	372.41	8.60	4.60
7	1008.96	18.94	14.94
8	925.23	18.82	14.82
9	865.93	19.18	15.18
10	991.18	21.30	17.30
11	975.87	21.34	17.34
12	1155.77	21.44	17.44
13	75.94	4.39	0.39
14	120.90	4.53	0.53
Max	1155.77	21.44	17.44
Min	75.94	4.39	0.39
Mean	551.40	12.07	8.07

Table 6: Correlation analysis of the studied metal concentration and indices.

	HPI	HEI	C_d
Cu	0.28493	0.232471	0.232471
Fe	-0.13795	-0.17139	-0.17139
Mn	**0.982306**	**0.991687**	**0.991687**
Zn	0.324095	0.409178	0.409178
HPI	1	**0.991048**	**0.991048**
HEI	**0.991048**	1	**0.991048**
Cd	**0.991048**	1	1

Significant levels >0.5

Table 7: Principal Component analysis for the surface water sample

Sites No.	PC 1	PC 2	PC 3
1	0.061618	-0.08742	0.032543
2	0.063501	-0.07648	0.18533
3	0.091098	0.2239	0.068677
4	0.086352	0.24878	**0.60069**
5	0.19721	0.043661	0.21548
6	0.19585	0.049666	0.066345
7	0.16849	-0.01117	-0.37295
8	**0.4535**	-0.08894	0.050419
9	**0.52236**	-0.15872	0.081089
10	0.17295	-0.48798	0.006428
11	**0.39394**	-0.34198	0.058621
12	0.05943	-0.16274	-0.47086
13	**0.37825**	**0.58683**	-0.40376
14	0.24606	**0.33311**	0.10861
Eigen value	55.491	0.426999	0.217741
Cumulative % of variance	98.85	99.61	100.00
% of variance	98.851	0.76065	0.38788

Loading values >0.3 were considered

Table 8: Average value of water quality parameters for each cluster

Parameters	Cluster 1 (1,2,3,4,5,6,7)	Cluster 2 (8,9,10,11,12,13,14)
Cu(ppb)	214.51	370.88
Fe(ppb)	339.98	278.48
Mn(ppb)	297.24	653.07
Zn(ppb)	2124.62	5163.17