



Heavy metals pollution index (HPI) assessment through water analysis for Yamuna river water in Agra district (India)

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Abstract

The present study was conducted on heavy metal pollution index (HPI) of Yamuna river water in Agra district U.P. (India) at sites viz., A1, A2, A3, A4 and A5 for summer and post-rainy seasons. Mean concentration of heavy metals followed the order Zn > Fe > Cu > Ni ≥ Mn > Cr > Pb > Cd in summer and Zn > Fe > Mn > Cu > Ni > Cr > Pb > Cd in post-rainy seasons. Zn and Cu were within permissible limit for drinking water quality at all sites in both seasons. Fe, Zn, Cr and Mn increased during post-rainy season against their covalent index. Mean heavy metal pollution index (HPI) for each sampling site reflected highest pollution at A4 site. Mean HPI for Yamuna river water in summer (261) decreased conspicuously in post-rainy season (92.5). Metal quality index (MQI) values were highest at A4 site i.e., 23.15 in summer and 22.0 in post-rainy seasons. Pearson's analysis showed significant positive correlation among all heavy metals.

Keywords: Heavy metal pollution index, analysis, Yamuna river water, Agra

Introduction

Rapid urbanization, industrialization and population growth in burgeoning cities has led to increased flux of heavy metals laden wastewater into India's rivers traversing through these cities^[1]. Heavy metals can enter river systems mainly from point and non-point sources i.e., effluents of industrial activities, domestic wastewater, runoff from agricultural fields and urban areas which supply huge quantities of inorganic ions and heavy metals^[2]. Heavy metals such as cobalt (Co), copper (Cu), chromium (Cr), iron (Fe), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) are required to maintain various biochemical and physiological functions in living organisms when in very low concentrations, however, they become toxic when exceed certain threshold concentrations^[3]. Whereas nonessential heavy metals such as aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), bismuth (Bi), cadmium (Cd), gallium (Ga), germanium (Ge), gold (Au), indium (In), lead (Pb), lithium (Li), mercury (Hg), platinum (Pt), silver (Ag), strontium (Sr), tellurium (Te), thallium (Tl), tin (Sn), titanium (Ti), vanadium (V) and uranium (U) are toxic even at very low concentration^[4]. Monitoring of heavy metal contamination in rivers is important because heavy metals pose threat to aquatic life, human health and to the environment due to biomagnifications and their toxicity^[5,6]. The interpretation of spatial and seasonal concentration of Heavy metals pollution Index (HPI) through water assessment analysis for Yamuna river water in Agra district, U.P. (India) can be useful in assessment of degree of pollution load and water quality trend of a river^[7,8]. Heavy metals pollution index (HPI) of a Yamuna river water can be a useful tool for regulatory agencies to make necessary policies and decisions regarding pollution abatement and resource management. The metal quality indices have been computed to assess the suitability level of water resources for drinking with respect to metals^[9]. Pearson's correlation analysis can be an effective tool for identification of

pollution sources, to apportion natural versus anthropogenic or mixed contributions^[10,11].

Yamuna river is the life artery of Agra district in Uttar Pradesh, (India) representing the main freshwater resource required for meeting domestic, industrial and irrigation water demands. The catchment area of Yamuna river water in Agra is highly urbanized and is networked by several drains. Fort drain is the largest drain that discharges a heavy load of pollutants into the river. Water quality evaluation of Yamuna river with respect to heavy metals is very important to realize the feasibility of its use for drinking. The river Yamuna has been monitored several times for the presence of heavy metals in various cities^[12]. However, in present study first time an attempt has been made to evaluate the current heavy metal (Fe, Pb, Cd, Cr, Cu, Ni, Mn) based water quality of Yamuna's stretch in Agra using indices i.e., heavy metal pollution index (HPI), metal quality index (MQI)^[13] and Pearson's correlation analysis.

Materials and Methods

Water samples were collected from five sites i.e., A1, A2, A3, A4 and A5 along the Yamuna river water stretch in Agra district, U.P. (India) during summer (May 2024) and post-rainy seasons (October 2024). Sites A2, A3 and A4 were lying inside the municipality zone of Agra, hence, these sites carried wastes of various municipality drains discharging into Yamuna. Whereas, A1 and A5 sites were lying outside the municipality zone and 5 Km upstream and downstream of the first and last municipality drains, respectively. The samples collected from each site consisted of 3 composite samples taken from 1 foot below the water surface using acid washed 500 ml polyethylene bottles to avoid unpredictable changes in characteristics. Water samples collected were placed at 4°C in an ice-jacket and transported to the laboratory immediately for further analysis. The collected samples were acidified with concentrated nitric acid to a pH below 2.0 to minimize precipitation and adsorption on bottles walls as required by

the standard procedure. The concentrations of heavy metals were determined using an atomic absorption spectrometry (PerkinElmer, 3300/96, MHS-10) after acid-digestion procedure for heavy metals analysis as per APHA (2012). All analyses were carried out in triplicate, and the results were expressed as the mean.

The HPI shows overall quality of water with respect to content of heavy metals. The critical HPI value is 100. The weighted arithmetic average of the concentrations was used to calculate HPI values using the Eq. 1 [14].

$$HPI = \frac{\sum_{i=1}^n w_i Q_i}{\sum_{i=1}^n w_i} \quad (1)$$

Where W_i is the unit weightage defined as reciprocal value of S_i where S_i is the maximum permissible limit for drinking water given and n is the number of parameters considered. Q_i is the sub-index of the i th parameter, and calculated by Eq. 2

$$Q_i = \sum_{i=1}^n \frac{M_i}{S_i} \times 100 \quad (2)$$

Where, M_i is the monitored value of heavy metal, S_i is the standard value of the parameter, in ppm ($\mu\text{g/L}$).

The higher the concentration of a metal compared to its respective maximum permissible limit (S_i), the worse the quality of the water. MQI value >1 is a threshold of warning the MQI is calculated by Eq.3

$$MQI = \sum_{i=1}^n M_i/S_i \quad (3)$$

The data were statistically analyzed using the SPSS 20.0 statistical software package to calculate average, standard deviation, Pearson's correlation coefficient and level of significance. Level of significance was calculated at $p < 0.05$.

Results and Discussion

The concentrations of eight heavy metals analysed for summer and post-rainy seasons and some basic statistics are shown in Table-1. The mean concentration of heavy metals in Yamuna water followed the order Zn ($1660 \mu\text{g l}^{-1}$) $>$ Fe ($420 \mu\text{g l}^{-1}$) $>$ Cu ($256 \mu\text{g l}^{-1}$) $>$ Ni ($166 \mu\text{g l}^{-1}$) \geq Mn ($162 \mu\text{g l}^{-1}$) $>$ Cr ($40 \mu\text{g l}^{-1}$) $>$ Pb ($34 \mu\text{g l}^{-1}$) $>$ Cd ($5 \mu\text{g l}^{-1}$) in summer and Zn ($2480 \mu\text{g l}^{-1}$) $>$ Fe ($608.5 \mu\text{g l}^{-1}$) $>$ Mn ($417 \mu\text{g l}^{-1}$) $>$ Cu ($185.8 \mu\text{g l}^{-1}$) $>$ Ni ($86.6 \mu\text{g l}^{-1}$) $>$ Cr ($71 \mu\text{g l}^{-1}$) $>$ Pb ($12.7 \mu\text{g l}^{-1}$) $>$ Cd (0.8) in post-rainy season. The concentration of all heavy metals was highest at A4 site because it is positioned downstream of the biggest drain of Agra i.e., Fort Drain which carried waste discharged from most of the chemical and fertilizer industries and residential areas of the city. Except Zn-Cu-Mn in summer and Zn-Cu in post-rainy season, all other heavy metals inside the municipality zone were above maximum permissible limits for drinking water quality given. The concentrations of different heavy metals increased continuously from A1 to A4 sites but decreased conspicuously at A5 during both seasons which may be due to the fact that A5 site being located 5 Km downstream of last municipality drain of the city, the distance provided sufficient time for heavy metals to settle down from dissolved phase to the bed sediments of river. During transportation of heavy metals in the Yamuna river water, it may undergo dissolution, precipitation and sorption [15].

In summers, Fe concentration was found 1.5 to 2.3 times higher than maximum permissible limit for drinking water quality from A2 to A4 sites, whereas within limits at A1 and A5 sites. However, in post-rainy season mean Fe concentration increased 1.4 times and reported 1.1 to 3.5 times higher than maximum permissible limit at all sites except at A1. High Fe levels can be accounted to municipal and metal industry waste waters. Pb was found 2 to 6 times higher than maximum permissible limit for drinking water quality at all sites in summers, whereas 2 to 3 times higher between A2 to A4 sites in post-rainy season. Source of Pb pollution may be lead acid batteries manufacturing industries. Cd was 1.3 to 27 times higher than maximum permissible limit for drinking water quality from A2 to A5 sites in summers and 1.3 times higher at only A4 site in post-rainy season. Its source was wastewater coming from electroplating and painting industries located in the city. The concentrations of Zn and Cu were found within permissible limit for drinking water quality at all sites in both seasons which indicated that they were not significant source of pollution in Yamuna river. In summer, Cr concentration was reported 1.6 times higher than maximum permissible limit for drinking water quality at A4 site, whereas within the limit at other sites. However, its mean concentration increased 1.8 times in post-rainy season and found 1.7 and 3.2 times higher than maximum permissible limit at A3 and A4 sites, respectively.

The high levels of Cr may be due to prominence of leather tanning industries in the city. Ni was reported 6 to 11.5 times higher than maximum permissible limit for drinking water quality at all sites in summer, whereas its mean concentration decreased significantly in post-rainy season and was reported 3.4 to 7.8 times higher than maximum permissible limit between A2 to A5 sites. The presence of stainless steel and refining industries in city contributed to high level of Ni in river. Mn concentrations were found under the maximum permissible limit for drinking water quality at all sites in summer, whereas its mean concentration increased by 2.6 times in post-rainy season and found 1.12 to 2.6 times higher than maximum permissible limit for drinking water quality between A3 to A5 sites.

The concentration of Pb, Cd, Cu and Ni decreased in post-rainy season due to dilution effect, whereas concentration of Fe, Zn, Cr and Mn increased which can be accounted to desorption of these metals from sediments due to dilution. Heavy metals enter into the rivers as inorganic complexes or hydrated ions, which are easily adsorbed on surface of sediment particles and constitute the labile fraction [16]. The increase in mean concentration of Fe, Zn, Cr and Mn in post-rainy season with respect to summer followed the order as Mn $>$ Cr $>$ Zn $>$ Fe which was inversely proportional to their covalent index Fe $>$ Zn $>$ Cr $>$ Mn. Higher the covalent index of a heavy metal stronger will be its adsorption [17] and hence lower will be its desorption due to dilution. Desorption of other heavy metals i.e., Pb, Cd, Cu and Ni also would have occurred but dilution was dominant factor, hence net result was decrease in concentration.

The mean concentrations of eight heavy metals (Pb, Cd, Fe, Zn, Mn, Cu, As and Hg) were taken for determination of the HPI values. Table-2 provides details of calculating HPI, W_i and Q_i values for both seasons. The critical value of the heavy metal's pollution index is 100 [18]. The mean HPI for Yamuna river water in summer (261) decreased significantly in post-rainy season (92.5). Hence, overall HPI of Yamuna river water was 176.75 which was above critical limit.

The high HPI values were mainly due to industrial and domestic wastewater discharge into river. HPI of different sampling sites were compared to assess pollution load and assess the water quality for the selected sites (Table-3). Heavy metals pollution index (HPI) values were above the critical index limit at all sites in summer, whereas only at A4 site in post-rainy season. Also, from the values of mean HPI for each sampling site could be concluded that the

pollution load at sampling site A4 was most significant i.e HPI 412 in summer and 238.5 in post-rainy season. Another index, metal quality index, was used to estimate the metal pollution of Yamuna river water Agra for drinking use by computing all measured metals (Table-4). All sites along the studied stretch were seriously threatened with metal pollution for drinking (MQI > 1), MQI reached to 23.15 and 22.0 at site A4 in summer and post-rainy seasons, respectively.

Table 1: Heavy metal concentration in Yamuna river water at Agra at different sampling sites and statistical values for mean concentration of various heavy metals

Heavy Metals	Summer							Post-rainy seasons						
	Concentration (µ/l)					Mean	SD	Concentration (µ/l)					Mean	SD
	A1	A2	A3	A4	A5			A1	A2	A3	A4	A5		
Fe	200	450	540	680	230	420	204.6	252	672	738.4	1059	321.1	608.5	329.2
Pb	20	20	40	60	30	34	16.7	1	2.6	20	30	10	12.7	12.2
Cd	3	4	6	8	4	5	2	0.0	0.0	0.0	4.0	0.0	0.8	1.8
Zn	1200	1500	1800	2000	1660	1632	303.5	1440	1950	2700	4400	1920	2482.0	634.1
Cr	20	20	50	80	30	40	25.5	30	32	85	160	48	71.0	54.4
Cu	150	180	240	570	140	256	179.8	100	120	167	430	112	185.8	138.8
Ni	120	150	180	230	150	166	41.6	20	87	102	156	68	86.6	49.6
Mn	100	130	180	260	140	162	61.8	220	299	450	780	336	417.0	219.2

Table 2: Heavy metal pollution Index (HPI) calculations for Yamuna river water Agra based on mean heavy metal concentration in summer and post-rainy season

Heavy Metals	Si (µ/l)	Wi (1/Si)	Summer			Post-rainy season		
			Mean concentration (Mi, (µ/l))	Qi (Mi, Si *100)	Wi*Qi	Mean concentration (Mi, (µ/l))	Qi (Mi, Si *100)	Wi*Qi
Fe	300	0.0033	420	140	0.47	608.5	202.8	0.676111
Pb	10	0.1	34	340	34	12.7	127.2	12.72
Cd	3	0.33	5	166.67	55.56	0.8	26.7	8.888889
Zn	15000	6.66667E-05	1632	10.88	0.00073	2482.0	16.5	0.001103
Cr	50	0.02	40	80	1.6	71.0	142.0	2.84
Cu	1500	0.0007	256	17.07	0.0114	185.8	12.4	0.008258
Ni	20	0.05	166	830	41.5	86.6	433.0	21.65
Mn	300	0.003	162	54	0.18	417.0	139.0	0.463333

Table 3: Heavy metal pollution Index (HPI) calculations for Yamuna river water Agra at each sampling site in summer and post-rainy season

Sampling site	Summer	Post-rainy season
A1. Kailash Ghat	165.3	15.12
A2. Poiya Ghat	202.3	52.3
A3. Balkeshwar Ghat	302.3	98.3
A4. Hathi Ghat	412.20	238.5
A5. Taj Ganj	222.2	58.1
Mean HPI	261	92.5

Table 4: Pearson's correlation analysis of heavy metal concentrations at various sampling sites in Yamuna river water Agra

Sampling Sites	MQI	
	Summer	Post-rainy season
A1. Kailash Ghat	9.9	3.44
A2. Poiya Ghat	11.88	8.69
A3. Balkeshwar Ghat	16.88	13.05
A4. Hathi Ghat	23.15	22.04
A5. Taj Ganj	13.10	7.75

Table 5: Pearson's correlation analysis of heavy metal concentration at various sampling sites in Yamuna river water Agra

Heavy Metals		Pearson's correlation (r)						
		Pb	Cd	Zn	Cr	Cu	Ni	Mn
Fe	Summer	0.79	0.92	0.81	0.83	0.83	0.91	0.88
	Post-rainy season	0.81	0.76	0.91	0.85	0.85	0.95	0.88
Pb	Summer	1	0.97	0.90	0.99	0.92	0.96	0.98
	Post-rainy season	1	0.79	0.95	0.97	0.87	0.88	0.95
Cd	Summer		1	0.92	0.98	0.92	0.99	0.99
	Post-rainy season		1	0.70	0.91	0.98	0.78	0.92
Zn	Summer			1	0.88	0.76	0.94	0.92
	Post-rainy season			1	0.91	0.82	0.94	0.91
Cr	Summer				1	0.94	0.96	0.98
	Post-rainy season				1	0.97	0.88	0.99
Cu	Summer					1	0.93	0.94
	Post-rainy season					1	0.86	0.97
Ni	Summer						1	0.99
	Post-rainy season						1	0.93

Intermetallic relations for Yamuna river water Agra revealed that there were significant correlations (Pearson correlation tests, $p < 0.05$) between all the eight metals in both seasons (Table-5). Positive correlation between metals analysed at different sites showed either an association/interaction between the metals or similar sources of input^[19]. Strong correlation between two heavy metals may be an occurrence of strong dependence of both metals on the same causal factor^[20]. In conclusions, our study on heavy metal pollution of river Yamuna for Agra stretch shows that site A4 is highly polluted mainly due to discharge of Fort drain. Heavy metals pollution index (HPI) of river shows that Yamuna river water is critically polluted with heavy metals and unsafe for drinking in both summer and post-rainy seasons. MQI was >1 at all sites in both seasons also indicating high metal pollution. Pearson's correlation analysis showed that it can be an effective tool for the identification of the sources of the pollutants. The study has relevance in designing control measures and action plans for reducing pollutants influx into rivers. The results of the study should be taken earnestly by the concerned water resource management authorities and policy makers for pollution abatement of the Yamuna river water of Agra district U.P. (India).

References

1. Paul D. *Annals of Agrarian Science*,2017:15:278–286.
2. Pandey J, Singh R. *Applied Water Science*,2017:7:1669–1678.
3. Jaishankar M, Tseten T, Anbalagan N, Mathew BB, Beeregowda KN. *Interdisciplinary Toxicology*,2014:7:60–72.
4. Paul BT, Clement GY, Patlolla AK, Dwayne JS. *Molecular and Clinical Environmental Toxicology*,2012:101:133–164.
5. Ahmed MK, Shaheen N, Islam MS, Habibullah-al-Mamun M, Islam S, Mohiduzzaman M, *et al.* *Chemosphere*,2015:128:284–292.
6. Ali MM, Ali ML, Islam MS, Rahman MZ. *Environmental Nanotechnology Monitoring and Management*,2016:5:27–35.
7. Reza R, Singh G. *International Journal of Environmental Science and Technology*,2010:7:785–792.
8. Prasanna MV, Praveena SM, Chidambaram S, Nagarajan R, Elayaraja A. *Environmental Earth Sciences*,2012:67:1987–2001.
9. Ojekunle OZ, Ojekunle OV, Adeyemi AA, Taiwo AG, Sangowusi OR, *et al.* Evaluation of surface water quality indices and ecological risk assessment for heavy metals in scrap yard neighbourhood. *SpringerPlus*,2016:5:560.
10. Yalcin MG, Tumuklu A, Sonmez M, Erdag DS. *Environmental Monitoring and Assessment*,2010:164:311–322.
11. Manoj K, Padhy PK, Chaudhury S. *Bulletin of Environmental Pharmacology and Life Sciences*,2012:1:07–15.
12. Malik D, Singh S, Thakur J, Singh RK, *et al.* *International Journal of Current Microbiology and Applied Sciences*,2014:3:856–863.
13. Abdel-Satar AM, Ali MH, Goher ME. *The Egyptian Journal of Aquatic Research*,2017:43:21–29.
14. Mohan SV, Nithila P, Reddy SJ. *Journal of Environmental Science and Health Part A*,1996:31:283–289.
15. Abdel-Ghani NT, Elchaghaby GA. *International Journal of Environmental Science and Technology*,2017:4:451–456.
16. Vukovic D, Stankovic SJ, Vukovic Z, Jankovic K. *Journal of the Serbian Chemical Society*,2014:79:379–387.
17. Pal R, Rai JPN. *Applied Biochemistry and Biotechnology*,2009:160:945–963.
18. Milivojević J, Krstić D, Šmit B, Djekić V. *Bulletin of Environmental Contamination and Toxicology*,2016:97:737–742.
19. Miller JN, Miller JC. *Statistics and chemometrics for analytical chemistry*. Pearson Education Limited,2002:4th edition.
20. Ashraf MA, Maah MJ, Yusoff I. *The Scientific World Journal*,2012:1:1–11