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Heavy metals and geo-accumulation index development for groundwater of Mathura city, Uttar Pradesh

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ABSTRACT

Heavy metal pollution in urban areas of India is very severe and complex. This study has been conducted to assess the health risk of inhabitants by heavy metals (Cd, Mn, Fe, Cu, Pb, Zn, Ni, and Cr) through the groundwater intake of Mathura city of Uttar Pradesh, India. A total of 65 groundwater samples were collected, and these samples were analyzed for the presence of heavy metals (Cd, Mn, Fe, Cu, Pb, Zn, Ni, and Cr). The total concentration of heavy metals present in groundwater was in the order of Ni > Fe > Pb > Cr > Cd > Zn > Mn > Cu Sediment quality indicator such as heavy metal pollution index (HPI) and geo-accumulation index (I_{geo}) were also evaluated in addition to multivariate statistical techniques, such as Pearson correlation matrix. The HPI mean value has been found to be 66.61 indicating the groundwater quality is in poor condition. The I_{geo} results confirm the certain extent of heavy metals contamination in the groundwater of Mathura city with respect to Pb, Cd, Ni, Fe, and Cr. The correlation matrix of the heavy metals in the groundwater has also been evaluated. No significant correlations have been observed among most of these heavy metals, indicating different anthropogenic and natural sources of contamination.

Keywords: Heavy metals; Geo-accumulation index; Pearson correlation coefficient

1. Introduction

The concentration of metal in aquatic and terrestrial environments has rapidly augmented as a result of urbanization, agricultural and industrial progress, and the associated enlargement in the human population and their consumption of resources [1,2]. In the past few years, many regions of arid and semi-arid climate have been facing a problem regarding drought and groundwater contamination. Surface water is being polluted due to industrialization, unprecedented population growth, excess deforestation and extensive agriculture [3–7], and land transformation [8] on the quality of drinking water resources [9]. It has been noted that the major contamination of groundwater is due to human activities. The groundwater pollution is due to presence of heavy metals that makes a concern for the scientific society. Heavy metal contaminations have become a serious issue in many parts of the world [10]. Wastewaters have been

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used for agricultural irrigation in many parts of the world without accounting for its suitability and leading to soil degradation [11]. Heavy metals are menace to ecosystem, especially when dissolved in ionic form in water [12]. Trace elements are distributed in groundwater from a variety of natural and anthropogenic sources such as discharges from refineries, agriculture, industries, and vehicular emissions [13]. These toxic pollutants degrade the quality and transfers from recharge site to discharge site through aquifer groundwater movement. Undesirable and soluble content cannot be controlled after entering the surface [14,15]. Several researchers have studied heavy metal contamination in various Indian rivers to investigate the geochemical environment of sediments [16–18]. The occurrence of toxic metals in groundwater affects the lives of local inhabitants whose daily requirements depend upon these water sources [19].

Heavy metals such as Fe, Mn, Cu, Zn, Co, and Ni are commonly known as micronutrients and important for living system. However, variations in the concentration of these heavy metals can cause several diseases in humans [20]. Some heavy metals such as Cd, Pb, and Cr can be more dangerous even at low concentration. Due to their property of saturation, these heavy metals accumulate in the human body [21]. The zone in the downstream of Ganges and Brahmaputra river system, the Indo-Gangetic basin (IGB) aquifer system, is one of the imperative freshwater assets on the planet [22]. The fertile IGB is one of the copiously populated districts, and it underpins business in excess of 400 million individuals. With the expanded population development and increased agri-business activities, countless wells are abstracting groundwater from IGB aquifer system. A study conducted by MacDonald et al. [22] indicates that the expanding groundwater extraction in IGB prompts groundwater consumption in limited regions. Considering these factors in view, a study was planned with the objective to analyze the concentration of heavy metals in the groundwater of Mathura city of Uttar Pradesh, India, situated in IGB region. In order to evaluate the health effects of the study area, the heavy metals pollution index (HPI) and geo-accumulation index (I_{geo}) have been developed for the same. This study can also serve as a helping tool in designing and implementing effective groundwater management strategies.

2. Materials and methods

2.1. Study area description

Mathura area is flanked by Haryana in the north and Rajasthan in the west. Its population is about 2.5 billion (approximately) and is one of the most populated districts of Uttar Pradesh. Mathura is one of the seven sacred places for Hindu believers. The details of the area undertaken in this study are shown in Fig. 1. It lies between latitudes 27° 14′ and 27° 17′ North and longitudes 77° 17′ and 78° 12′ East and covers an area of about 3,339 km^2. Study region lies on the toposheet numbers 54E and 54I of Survey of India. Zone is plain nation with a couple of strike edges around Gobardhan (27° 30′ 77° 28′; 54E), Barsana (27° 39′ 77° 23; 54E), and Nandgaon (27° 43:77° 23; 54E). The plain is a piece of the Indo-Gangetic alluvial plain. Physiographically, the area is partitioned into older and newer alluvial plains.

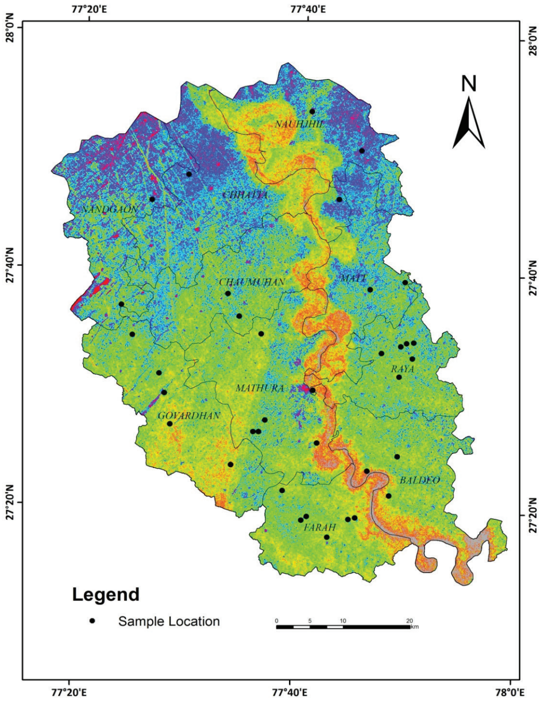

Fig. 1. Map of the sample location, Mathura district.

The older alluvial fields are level to tenderly undulating alluvial tract. Soil types commonly found are silty, sandy, and loamy soils. According to Central Ground Water Board (CGWB), India, the number of tube wells and bore wells reported in this region is 61,456. During pre-monsoon period, the water level (below ground level) is 2.65–14.34 m, and during post-monsoon, the levels are between 1.33 and 14.0 m (below ground level) [23].

2.2. Geological aspects of the study area

The study area forms a part of Gangetic Plain underlain by younger and older alluvium of quaternary age. Vindhyan sandstones are visible in the southwest of Mathura district. The alluvial deposits include silt, sand, clay, kankar, gravels, occasionally, thick bands of sticky clays, indurated sand, and their combinations in one of kind proportions (Table 1). The older alluvium is brown to yellowish brown in shade while the more new alluvium is light to grayish in shade with ample mica flakes. The older alluvium covers the major part of the vicinity. It forms higher surroundings and is unaffected with the aid of floods. The thickness of alluvium varies in the location, its miles reducing in southwestern area. The younger alluvium represents second generation of quaternary alluvium, forming depositional terrace.

Mathura has 103,770 canals, 164,294 private tube wells, and 161,342 ha of bore wells. Multiple aquifer groups (two) up to 258.47 m depth are found in the study area. Post monsoon: Rise 0.0300–0.3684 m/year (Jachonda Vrindavan). Post monsoon: Fall 0.0077–4.2387 m (Saunkh–Raya). During pre-monsoon period, the water level (below ground level) is 2.65–14.34 m, and during post–monsoon period, the levels are between 1.33 and 14.0 m (below ground level) [23].

Table 1
Geological succession of the study area [24]

Group	Age	Formation	Lithology
Quaternary	Holocene	Yamuna recent alluvium	Coarse grained, quartzofeldspathic sand reddish in color, occur in patches in the western part and micaceous grey sand
		Yamuna terrace alluvium	Composed of grey micaceous sand, clay, and over bank silt
		Mathura older alluvium	Composed of multicyclic sequence of clay, silt, and sand with calcrete
	Middle to Late Pleistocene	Older alluvium (Varansi alluvium)	Oxidized, khaki to brownish yellow silt, clay with kankar disseminations, and grey to brown fine to medium-grained sand
Proterozoic-III	Vindhyan Supergroup		Upper Bhander Sandstone, quartzite, phyllite, and shale group

To disentangle the sub-surface geology of the region in view of the exploratory boreholes information in all the boreholes, the bedrock has been experienced at variable profundity. The investigation of exploratory information has uncovered that the alluvial thickness is nearly low in western and southern parts. The thickness of alluvial material differs between 150 and 200 m. The alluvial thickness increment in north and northeast bound is between 250 and 300 m. In extreme western part in Sahi and Bhainsa, quartzite and slate having a place with Delhi system have been experienced, while in the middle parts of the area, limestone/shale having a place with Vindhyan system has been experienced. The resistivity overview completed by Geological Society of India, 1971, in sections of the area has uncovered extending of bedrock in northeastern parts of the region. It uncovers that clay prevails in western and southern parts. Potential aquifer beneath 10–15 m thick earth topping is available in northeastern parts of the area. Thickness of top clay layer increases southward. No prominent aquifer has been observed in western and southern parts of the district [23].

2.3. Methodology of this study

Groundwater samples were collected from 65 representative sites from the piezometer bore hole by the CGWB in various parts of the Mathura city. The water from the bore holes piezometer is withdrawn initially for the removal of the stagnant water from the aquifer. After the removal of this stagnant water, the sample was collected in pre-cleaned (1N-HCl) 1 L polyethylene bottle, and then all the samples were filtered through Whatman 0.45 micron pore size filter paper in a 100-mL polyethylene bottle that was pre-washed with double distilled water. These samples were acidified using ultrapure 65% nitric acid (0.5 mL/100 mL of water) to avoid possible concentration changes and were kept subsequently at temperatures below 4°C to avoid unpredictable changes in chemical composition [25]. The trace element analysis (Pb, Zn, Cd, Ni, Fe, Co, Cr, and Cu) was carried out by using atomic absorption spectrophotometer (PerkinElmer 800, Waltham, Massachusetts, USA). The analytical detection limits for Pb, Cd, Ni, Cr, and Cu were 2.1, 0.07, 3.6, 0.19, and 0.75 pg, respectively. All heavy metals determinations were made as per procedure laid down in standard methods [25]. The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, recovery of known additions, and analysis of replicates. All analyses were carried out in triplicate, and the results were expressed as the mean. Concentrations of various heavy metals in the ground of the study area are summarized in Table 4.

2.4. Heavy metal pollution index

HPI is a technique for the assessment of the quality of water with reference to the concentration of heavy metal. In computing, the HPI, considered unit weightage (W_i) as a value inversely proportional to the recommended standard (S_i). The HPI model is given by Eq. (1).

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} W_i \times Q_i}{\sum_{i=1}^{n} W_i} \tag{1}$$

where Q_i is the sub-index of the i-th parameter, W_i is the unit weightage of the i-th parameter, and n is the number of parameters, considered where M_i is the monitored value of heavy metal of i-th parameter, I_i is the desirable maximum value, and S_i is the standard value of the i-th parameter. The sub-index (Q_i) of the parameter is calculated by Eq. (2).

$$Q_i = \sum_{i=n}^{n} \frac{|M_i - I_i|}{\left[S_i - I_i\right]} \times 100 \tag{2}$$

where M_i is the monitored value of heavy metal of i-th parameter, I_i is the ideal value of the i-th parameter, and S_i is the standard value of the i-th parameter. The quantity $[M_i–I_i]$ indicates numerical difference of the two values, ignoring the algebraic sign that is the absolute value. The critical value of HPI for drinking water is 100, above this value is not suitable for drinking purposes [26,27]. The water quality categorization in terms of heavy metals concentration as HPI has been reported by Majhi and Biswal [27] is tabulated in Table 2.

2.5. Geo-accumulation index

I_{geo} was originally defined by Muller [28] in 1969, in order to determine and define metal contamination in sediments, by comparing current concentration with pre-industrial levels. It can be calculated by using Muller method as follows:

$$I_{geo} = \log_2 (C_i/1.5\ C_{ri}) \quad (3)$$

where C_i is the measured concentration of the examined metal i in the sediment and C_{ri} is the geochemical background concentration or reference value of the metal i. Factor 1.5 is used because of possible variations in background values for a given metal in the environment as well as very small anthropogenic influences. According to Al-Haidarey et al. [29], the reference samples were As: 13, Cd: 0.3, Co: 20, Cr: 100, Pb: 20, and Cu: 50 μg/g. In this study, we have used Cd as a sample reference metal to calculate the I_{geo} because Cd was considered that the distribution of Cd was not related to other heavy metals, and usually has a moderately high concentration in the groundwater. I_{geo} was distinguished into seven classes by Ismaeel and Kusag [30] as summarized in Table 3.

2.6. Pearson correlation coefficient

Pearson's correlation coefficient, when applied to a sample, is commonly represented by the letter r and may be referred to as the sample correlation coefficient or the sample Pearson correlation coefficient. We can obtain a formula for r by substituting estimates of the covariance's and variances based on a sample into the following formula:

$$r = \frac{\sum (x - X)(y - Y)}{\sqrt{\sum (y - Y)^2 \sum (x - X)^2}} \quad (4)$$

where x and y are the values whose correlation coefficient is to be calculated. X and Y are the mean values of x and y. The correlation coefficient is a measure of linear association between two variables. Values of the correlation coefficient are always between –1 and +1. A correlation coefficient is a statistical measure of the degree to which changes when one change to the value of another. In positively correlated variables, the value increases or decreases in tandem. Correlation coefficients are expressed as values between +1 and –1. A coefficient of +1 indicates a perfect positive correlation: a change in the value of one variable will predict a change in the same direction in the second variable. A positive correlation is a relationship between two variables such that their values increase or decrease together. The correlation between different metals of each area was calculated using Pearson coefficient.

Table 2
Status categories of HPI for categorizing the quality of water in terms of heavy metals concentration [27]

HPI	Quality of water
0–25	Very good
26–50	Good
51–75	Poor
Above 75	Very poor

Table 3
The degree of metal pollution in terms of seven enrichment classes [30]

I_{geo}	I_{geo} class	Sediment quality
0.0–0.0	0	Unpolluted
0.0–1.0	1	Unpolluted to moderately polluted
1.0–2.0	2	Moderately polluted
2.0–3.0	3	Moderately to highly polluted
3.0–4.0	4	Highly polluted
4.0–5.0	5	Highly to very highly polluted
5.0–6.0	>5	Very highly polluted

3. Results and discussion

Samples collected from 65 sampling sites of Mathura district were assessed for the total heavy metals concentrations. The heavy metals Cd, Pb, Ni, Cu, Zn, Mn, Fe, and Cr were determined in all the groundwater samples, and average values for the same are summarized in Table 4. Data from Table 4 indicate that the concentration of Cd, Pb, Ni, Cu, Zn, Mn, Fe, and Cr is observed to be 1.833, 2.29, 3.373, 0.04, 0.505, 0.105, 2.58, and 1.9 mg/L, respectively. However, the actual concentration of Cd, Pb, Ni, Cu, Zn, Mn, Fe, and Cr ranged as 0.912–3.631 mg/L, 0.62–5.888 mg/L, 1.506–5.124 mg/L, 0–0.44 mg/L, 0.223–0.815 mg/L, 0.0–0.74 mg/L, 0.94–4.8 mg/L, and 0.4–3.8 mg/L, respectively.

The statistical analysis of the analyzed samples for eight heavy metals has been carried out in terms of mean values, standard deviation, and maximum and minimum values as summarized in Table 5. However, the mean concentration of heavy metals as calculated is depicted through Fig. 2. Perusal of the data from Fig. 2 designates the order of these heavy metals as Ni > Fe > Pb > Cr > Cd > Zn > Mn > Cu. Therefore, it can be inferred that the Ni average concentration of 3.372 mg/L is observed to be maximum while 0.04 mg/L as average concentration of Cu is observed to be minimum value as compared with all the assessed heavy metals.

The average concentration of Nickel in water is observed to be higher than other metals as a consequence of direct discharging of untreated wastes from industries. In the residential areas, the local dumping is expected to be the main source for Nickel metals. The highest Ni concentration (5.124 mg/L) was observed in Village Palson, Goverdhan Block in Mathura. The enhanced Ni concentrations in water samples can be attributed to the occurrence of ultramafic rocks in the area [31]. The highest Pb concentration (5.89 mg/L) was observed in groundwater sample collected from Koshi, Nandgaon Block. Lead is released from smelting, motor-vehicle exhaust fumes, and from corrosion of lead pipe work.

The highest Cd concentration of 3.631mg/L has been observed in groundwater sample collected from Barsana, Nandgaon Block. Cadmium occurs naturally in ores together with zinc, lead, and copper. Cadmium compounds are used as stabilizers in polyvinyl chloride products, color pigment, several alloys and, now most commonly, in re-chargeable nickel–cadmium batteries. Natural as well as anthropogenic sources of cadmium, including industrial emissions and the application of fertilizer and sewage sludge to farm land, may lead to contamination of soils, and to increased cadmium uptake

Table 4
Determined average concentration values of heavy metals in samples taken from all the locations of the study area

S. no.	Sample location details	Concentration (mg/L)							
		Cd	Pb	Ni	Cu	Zn	Mn	Fe	Cr
1	Raya 2, Raya Block	0.912	5.003	2.291	0.399	0.223	0.307	2.208	1.195
2	Naurangia Jagatiya	1.245	0.313	3.089	0	0.264	0.362	1.734	1.515
3	Village Usfar, Mathura Block	1.485	3.402	3.652	0.036	0.297	0.295	1.301	1.108
4	Nagla Jharela, Nandgaon Block	1.309	1.982	1.506	0	0.516	0.235	0.94	0.872
5	Khuma, Raya Block	1.405	2.651	1.794	0	0.594	0.276	1.329	0.428
6	Goverdhan 2, Goverdhan Block	2.284	3.563	2.212	0.116	0.613	0	1.391	1.078
7	Farah B.D.O, Farah Block	1.746	0.307	2.502	0.221	0.621	0.021	1.127	0.382
8	Beri, Farah Block	1.765	1.211	3.238	0.203	0.638	0.025	1.718	2.315
9	Falain, Chhatta Block	1.731	0.381	1.827	0	0.624	0.116	2.808	0.878
10	Simana, Raya Block	2.26	0.309	3.249	0	0.551	0.083	1.521	1.321
11	Mathura Refinery, Mathura	2.087	2.073	1.981	0.103	0.504	0.069	2.281	1.62
12	Village Palson, Goverdhan Block	1.813	2.83	5.124	0.183	0.483	0.115	1.782	1.07
13	Aajai Khurd, Chaumauhan Block	2.252	1.994	2.734	0.116	0.515	0.081	2.402	1.863
14	Akbarpur, Chaumauhan Block	1.853	0.623	3.081	0	0.533	0.052	2.339	1.286
15	Haripur, Nandgaon Block	2.298	1.178	3.083	0	0.551	0.034	1.8	1.243
16	Sersha, Farah Block	2.037	1.166	2.421	0	0.642	0.045	2.84	0.85
17	Jamalpur, Farah Block	1.255	0.918	2.663	0	0.672	0.016	2.023	1.295
18	Surir Kalan, Matt Block	1.363	2.001	2.961	0	0.681	0.147	2.068	1.128
19	Village Mukdumpur, Mathura block	1.901	1.971	3.546	0	0.687	0.073	2.027	0.895
20	Village Neemgaon, Goverdhan Block	1.511	2.62	4.714	0	0.708	0.005	2.792	1.919
21	Pirsua, Raya Block	1.688	3.546	3.488	0	0.476	0.047	1.89	1.489
22	Behrana, Raya Block	1.738	2.612	3.131	0	0.518	0.052	2.294	1.383
23	Neemgaon, Matt Block	2.316	1.637	2.713	0	0.564	0	2.089	1.57
24	Bazzna, Naujhil Block	2.333	0.807	2.309	0	0.496	0	2.588	1.49
25	Nagla Sajna, Baldeo Block	1.842	1.645	3.671	0	0.588	0.072	1.437	1.669
26	Village Paintha, Goverdhan Block	1.595	2.689	3.559	0.053	0.427	0.12	2.916	2.043
27	Raheempur, Farah Block	1.601	1.718	3.665	0.088	0.439	0.097	2.621	0.678
28	Yamuna River, Mathura City	1.667	1.823	2.639	0.187	0.413	0.151	2.05	2.643
29	Jabra, Matt Block	1.523	2.105	2.831	0	0.544	0.094	2.207	1.329
30	Daulatpur, Baldeo Block	2.258	2.259	3.482	0	0.415	0	2.747	2.519
31	JAIT, Mathura Block	2.001	1.878	3.197	0	0.409	0	3.036	1.128
32	Village Sonkhi, Goverdhan Block	1.898	2.038	3.395	0	0.418	0.11	2.856	1.841
33	Habeebpur, Baldeo Block	1.925	0.158	2.524	0	0.465	0.137	4.804	1.288
34	Baldeo B.D.O, Baldeo Block	1.704	1.747	2.913	0.145	0.543	0.063	3.065	2.289
35	Hasanpur, Naujhil Block	1.901	2.541	2.981	0.183	0.302	0.057	2.645	2.204
36	Village Usfar, Mathura block	1.961	1.488	3.874	0	0.326	0.003	2.658	1.418
37	Village Lalpur, Goverdhan Block	1.805	3.019	3.304	0.028	0.328	0.117	2.889	2.21
38	Gidoh, Nandgaon Block	1.591	3.301	4.687	0.442	0.329	0.08	2.578	2.419
39	Makdoompur, Naujhil Block	2.634	2.593	3.309	0	0.369	0.047	3.258	1.959
40	Shergarh 1, Chhatta Block	2.527	1.719	3.034	0	0.353	0.14	3.004	1.987
41	Nandgaon, Nandgaon Block	2.238	2.701	4.363	0	0.478	0.113	2.24	2.781
42	Village Son, Goverdhan Block	2.095	3.444	2.851	0	0.529	0.023	2.66	1.055
43	Matt 1, Matt Block	2.319	4.281	3.177	0.157	0.537	0.073	2.816	2.259
44	Charmarpur, Baldeo Block	2.227	3.623	4.273	0	0.547	0.17	2.908	2.732
45	Mathura B.D.O, Mathura Block	1.701	4.307	4.261	0	0.442	0.074	2.8	2.201
46	Narisemri, Chaumauhan Block	1.818	4.914	4.487	0	0.815	0.072	3.087	2.062
47	Nunera, Raya Block	1.549	5.103	4.085	0	0.556	0.257	2.848	2.128
48	Koshi, Nandgaon Block	1.448	5.888	3.602	0	0.483	0.144	2.688	2.71

(*continued*)

Table 4 (*continued*)

S. no.	Sample location details	Concentration (mg/L)							
		Cd	Pb	Ni	Cu	Zn	Mn	Fe	Cr
49	Shahpur, Raya Block	1.505	2.611	3.927	0	0.465	0.05	2.489	2.091
50	Bijauli, Matt Block	1.343	1.616	4.076	0	0.352	0.106	2.599	2.707
51	Gohari, Chhatta Block	1.632	1.076	4.176	0	0.447	0.102	3.164	2.045
52	Chhatta, Chhatta Block	1.797	1.405	3.258	0	0.45	0.091	3.13	2.299
53	Hothoda, Baldeo Block	3.208	1.007	4.171	0	0.479	0.045	3.327	2.061
54	Paigaon, Chhatta Block	0.928	3.122	3.529	0	0.608	0.114	3.041	1.752
55	Chaumauhan B.D.O, Block	1.001	1.707	3.881	0	0.505	0.078	3.5	2.478
56	Nagla Bharau, Raya Block	1.528	2.296	3.797	0	0.51	0.032	3.539	2.393
57	Chhinpari, Naujhil Block	1.438	2.973	3.984	0	0.51	0.123	3.529	3.408
58	Sabji Mandi Mathura Block	1.276	3.999	3.804	0	0.481	0.015	3.329	3.402
59	Andua, Matt Block	1.721	3.484	4.522	0	0.447	0.171	3.289	2.711
60	Barsana, Nandgaon Block	3.631	1.703	3.468	0	0.559	0.119	3.047	3.114
61	Tarauli Janvi, Chaumauhan Block	1.435	2.843	4.011	0	0.677	0.089	3.04	2.314
62	Village Palikhera, Block	1.152	2.751	3.477	0	0.661	0.74	3.19	3.803
63	Hussainee, Chhatta Block	1.186	1.079	3.797	0	0.667	0.095	3.114	2.104
64	Shehi, Goverdhan Block	2.435	2.764	3.901	0	0.475	0	3.179	2.721
65	Sathoha, Mathura Block	2.128	2.806	3.979	0	0.49	0.23	3.741	2.001

Table 5
Statistical analysis of the determined metals concentration in all sampling locations

Metals	Mean (mg/L)	Standard deviation	Maximum	Minimum
Cd	1.8332	0.4969	3.631	0.912
Pb	2.289	1.321	5.888	0.62
Ni	3.372	0.7616	5.124	1.506
Cu	0.04	0.0913	0.44	0
Zn	0.5047	0.1172	0.815	0.223
Mn	0.105	0.113	0.74	0
Fe	2.58	0.7081	4.8	0.94
Cr	1.9	0.7371	3.8	0.4

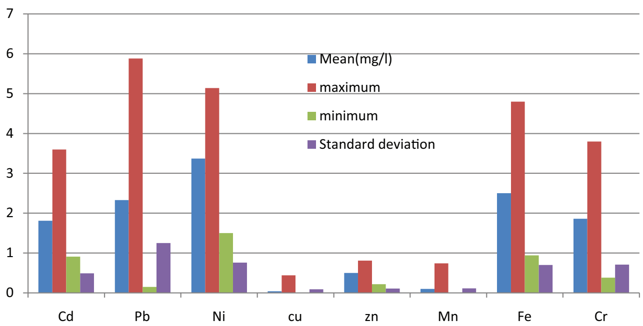

Fig. 2. Comparison of variation of heavy metals concentration at all locations.

by crops and vegetables, grown for human consumption. Chromium is a low-mobility element, especially under moderately oxidizing and reducing conditions and near-neutral pH values. Cr^{6+} adsorption decreases with increasing pH, and Cr^{3+} adsorption increases with increasing pH. On the other hand, Cr (VI) is toxic for biological systems [32].

The highest Cr concentration of 3.8 mg/L is observed in groundwater sample collected from the Village Palikhera in Mathura Block. The source of Cr appears to be anthropogenic from the existing tannery industries, where they are using chromium and its compounds. The highest Fe concentration of 4.8mg/L has been observed in Habeebpur, Baldeo Block in Mathura. Using the abovementioned assessed data, HPI has been evaluated in this study as per the method prescribed by Milivojević et al. [26]. In order to calculate the HPI of the water, the mean concentration value of the selected metals (Pb, Cd, Fe, Ni, Mn, Zn, Cr, and Cu) has been taken into account details for the calculations of HPI. The values of unit weightage (W_i) and standard permissible value (S_i) have been obtained accordingly and is presented in Table 6. Also, the determined values of HPI can be compared with the standard values tabulated in Table 2 for categorizing the water quality of the particular area. In this study, the HPI value is found to be 66.61. Perusal of the data summarized in Table 6 indicates that the groundwater quality is poor as per the values in Table 2 prescribed by Majhi and Biswal [27]. According to the study by Singh and Kamal [33], the groundwater quality of Goa region is found to be better than Mathura city with HPI values 1.5 and 2.1 in the monsoon and post-monsoon seasons, respectively, indicating that the groundwater is less polluted with heavy metals. The results of Gupta et al. [34] also indicate the similar result that drinking water of Dehradun, Uttarakhand, poses no risk due to heavy metal pollution with HPI values 24.5656 and 29.157 in the pre-monsoon and post-monsoon seasons, respectively.

Also using inverse distance weight interpolation in a geographic information system environment, the water quality map of the study area has been prepared in terms of HPI values. The water quality contamination and deterioration of Mathura district can be shown through Fig. 3. It represents water quality map based on HPI. The quality is classified in four groups accordingly as per the values mentioned in Table 2. In the study area, the orange patches observed in the western, southern, and eastern parts of the area showing pathetic and poor quality condition of groundwater. However, minor patches of good quality water can be observed in the central part of Mathura showing the situation in control. Therefore, from Fig. 3, it can be inferred that the water quality in most of the areas of the Mathura district is observed to be very poor indicating the contamination and pollution of groundwater due to rapid urbanization, unaccounted discharging water effluents from day-to-day activities.

The correlation matrix of the heavy metals in the groundwater has been evaluated and summarized in Table 7. Perusal of the data from Table 7, it can be observed that there is a positive correlation between the heavy metals. The correlation between Cd and Fe, Pb and Ni, Pb and Cu, Pb and Mn, Pb and Fe, Pb and Cr, Ni and Fe, Ni and Cr, Mn and Cr, and Fe and Cr is observed to be positive. It can be seen that, if there is increase in one metal concentration, then the concentration of other metals also increases. This may be due to the quantum of industrial wastes seepage continuously into the groundwater through soil and sub soil strata. The significant positive correlations within these metals reveal that their common source is industrial contamination and also the sinks in soils of the study area. The correlation coefficient between Cd and Cr is found to be 0.10. While Fe and

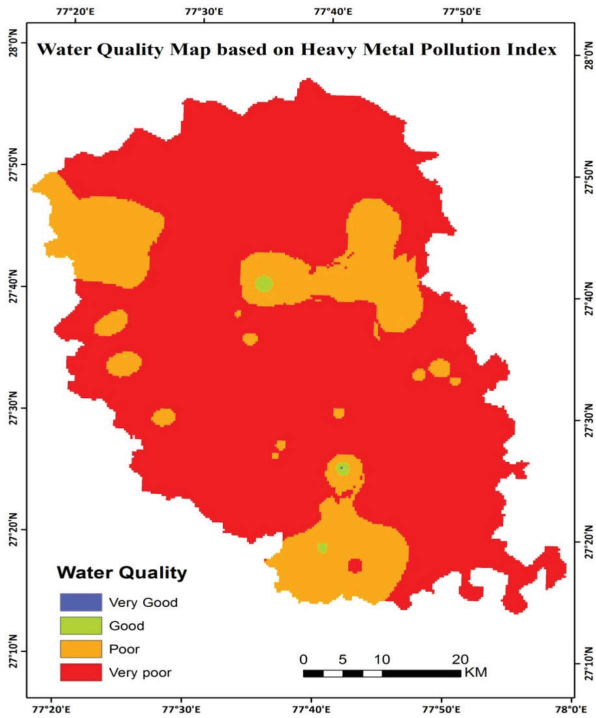

Fig. 3. Water quality map based on HPI values of this study.

Table 6
Heavy metal index development for the study area

Heavy metals	Mean concentration, M_i (mg/L)	Permissible limit for drinking water, S_i (mg/L)	Desirable maximum value, Ii (mg/L)	Unit weight, W_i ($1/S_i$)	Subindex, Q_i	$W_i \times Q_i$
Cd	1.833	–	0.003	–	–	–
Pb	2.289	–	0.010	–	–	–
Ni	3.372	–	0.020	–	–	–
Cu	0.041	1.50	0.050	0.666	0.626	0.41
Zn	0.505	15.0	5.00	0.066	44.950	2.96
Mn	0.105	0.30	0.100	3.333	2.500	8.33
Fe	2.580	1.0	0.300	1.000	325.710	325.71
Cr	1.860	–	0.050	–	–	–
				$\sum W_i = 5.065$		$\sum W_i \times Q_i = 337.41$
HPI = 66.61						

Table 7
Developed correlation matrix of heavy metals analysis in this study

Heavy metals	Cd	Pb	Ni	Cu	Zn	Mn	Fe	Cr
Cd	**1.00**							
Pb	–0.17	**1.00**						
Ni	–0.02	**0.33**	1.00					
Cu	–0.12	0.17	–0.08	**1.00**				
Zn	–0.03	–0.06	–0.05	–0.28	**1.00**			
Mn	–0.35	0.16	–0.04	0.02	–0.10	**1.00**		
Fe	0.10	0.11	**0.35**	–0.24	–0.07	–0.02	**1.00**	
Cr	0.04	**0.33**	**0.51**	–0.07	–0.10	0.18	0.53	**1.00**

Note: Bold values indicate the positive correlation between heavy metals.

Cr formed another highly correlated pair with a correlation coefficient of 0.53, suggesting their probable origination from some common sources. Mn exhibited moderate correlations with Cr (0.18). Fe and Mn occur naturally in abundant levels and are thus barely affected by human activities. Except Cu and Zn that shows statistically insignificant negative correlation with Cr, the rest of heavy metals contaminants show a considerable positive correlation with Cr.

The test of significant as calculated is observed to be $r > \pm 0.05$. However, in some cases, there are no significant correlations among most of these heavy metals, suggesting that these metals are not associated with each other and their identical behavior during transport in estuarine environment. Furthermore, these metals might have different anthropogenic and natural sources in groundwater of Mathura. The correlation of each heavy metal has been calculated and is shown through Figs. 4(a)–(f). Fig. 4(a) shows the Cd correlation with other heavy metals. It can be concluded from Fig. 4(a) that Cd shows negative correlation with Pb (–0.17), Cu (–0.12), Mn (–0.35), and positive correlation with Fe.

Perusal of the data from Fig. 4(b) indicates the Pb correlation with other heavy metals. It can be concluded from Fig. 4(b) that Pb shows positive correlation with Ni (0.33), Cu

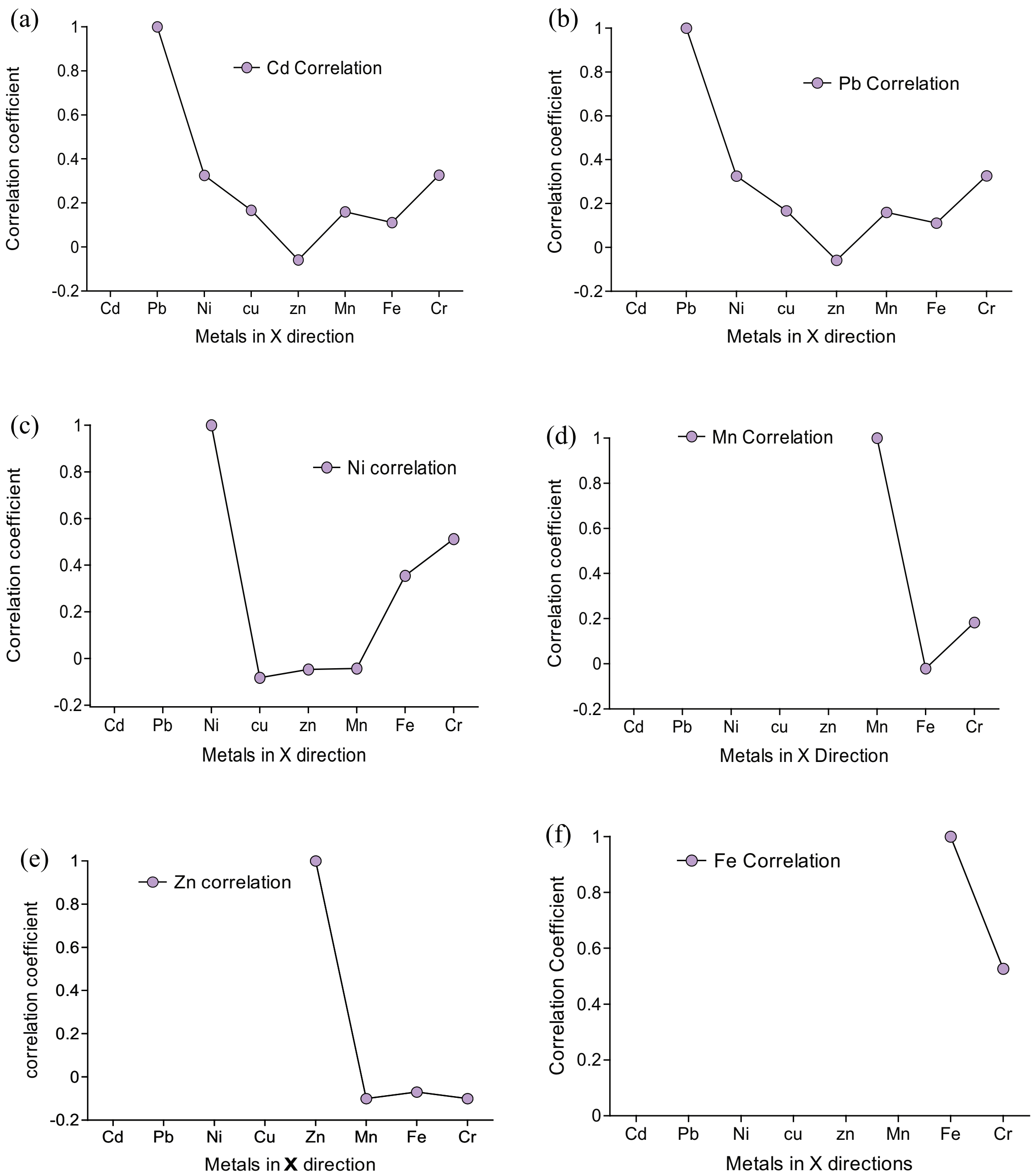

Fig. 4. Correlation of heavy metals in this study: (a) Cd, (b) Pb, (c) Ni, (d) Mn, (e) Zn, and (f) Fe.

Table 8
Correlation of heavy metals with HPI

Heavy metals	Cd	Pb	Ni	Cu	Zn	Mn	Fe	Cr	HPI
Cd	1								
Pb	–0.25939	1							
Ni	–0.03178	0.325757	1						
Cu	–0.13499	0.166628	–0.08197	1					
Zn	–0.11981	–0.05836	–0.04673	–0.28287	1				
Mn	–0.24767	0.159615	–0.0425	0.018213	–0.10029	1			
Fe	0.04267	0.111141	0.354295	-0.24251	–0.06786	–0.02117	1		
Cr	0.018807	0.326341	0.512142	–0.06959	–0.09961	0.183321	0.526567	1	
HPI	–0.03375	0.105021	0.099254	–0.21577	–0.01975	0.628313	0.50318	0.433115	1

Table 9
Geo-accumulation index (I_{geo}) values as determined in this study

Heavy metals	I_{geo}	Degree of pollution
Cd	2.02	Moderate to high
Pb	2.34	Moderate to high
Ni	2.90	Moderate to high
Cu	–3.64	Unpolluted
Zn	0.16	Unpolluted to moderate
Mn	2.12	Moderate to high
Fe	2.52	Moderate to high
Cr	2.07	Moderate to high

(0.17), Mn (0.16), Fe (0.11), and Cr (0.33). Fig. 4(c) shows the Ni correlation with other heavy metals. It can be concluded from Fig. 4(d) that Ni shows negative correlation with Cu (–0.08) and positive correlation with Fe (0.35) and Cr (0.51). Fig. 4(e) shows the Zn correlation with other heavy metals. It can be concluded from Fig. 4(e) that Zn shows negative correlation with Mn, Fe, and Cr.

The correlation of HPI with heavy metals has also been evaluated indicating the major influence of Mn, Fe, Cr, and Pb on HPI (Table 8).

However, I_{geo} classes of abovementioned heavy metals have also been evaluated. The estimated I_{geo} classes for eight heavy metals are summarized in Table 9. Data from Table 9 reveal that in terms of I_{geo} values, the heavy metals Cd, Pb, Ni, Fe, and Cr fall into Class 3 (Table 2.) This indicates that the water in these stations of the study area is observed to be moderately to highly contaminated by the effect of these heavy metals. Also, the evaluated I_{geo} values of Zn reveals the fact that the Zn falls into Class 1 category thus indicating the degree of I_{geo} from unpolluted to moderately polluted. Similarly the heavy metals Cu and Mn falls in Class 0 which indicates that the water in these stations in not contaminated with these heavy metals.

4. Conclusion

In this study, the mean concentration of heavy metal in groundwater is found to be in the order of Ni > Fe > Pb > Cr > Cd > Zn > Mn > Cu. The concentration of most of the heavy metals Ni, Fe, Pb, Cr, Cd, and Mn in groundwater was not found within the permissible limits set by Bureau of Indian Standards in Mathura city due to rampant agricultural activities and disposal of wastewater from paint industries, refineries, and from industrial effluents of Wazirabad. No significant correlation has been observed among the evaluated heavy metals, suggesting that these metals are not associated with each other indicating different anthropogenic and natural polluting sources of groundwater in study area. The results of I_{geo} confirm the extent of metal contamination in groundwater of Mathura city particularly with regard to Pb, Cd, Ni, Fe, and Cr that causes moderate to high pollution in most of the study area. The developed HPI model is found to be promising and is proved to be a useful tool in evaluating the overall pollution level of groundwater in terms of heavy metals. Finally, from the calculated HPI values, it can be concluded that the drinking water in the study area poses chronic health risk. As the groundwater quality is severely contaminated, it is recommended to the concerned authorities and institutions to carry out immediate remedial measures for conservation of groundwater, by preparing and implementing an immediate conservation plan.

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