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ORIGINAL ARTICLE

Examining the groundwater quality in the vicinity of a coal-based Thermal Power Plant in India necessitates inclusion of metal pollution indices

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ABSTRACT

Groundwater (GW) quality near coal-based thermal power plant (TPP) at Dadri in India were examined for physico-chemical properties. Concentration of heavy metals (HMs) Fe, Zn, As, Cu, Cd, Cr and Pb were evaluated in GW thrice a year at six sites, during two consecutive years. Altered contributions of individual HM and seasonal variations were noted. The pH, total hardness and TDS were within the limits of Bureau of Indian Standards (BIS, 2012) standards of drinking water quality. Nitrate levels were high in GW. The Contamination Index (C_d) and Heavy metal evaluation index (HEI) suggest 33%, 50% and 17% of the sites to have low, medium and high metal contamination, respectively. The higher HEI values largely appear to be due to high Pb concentrations. The Heavy metal pollution index (HPI) for 67% locations were dominantly of medium class while 33% were recognized with high class HPI. The WQI of the GW in the region near TPP reflects seasonal variations and that through the water quality appears to be fit for domestic use yet this is not true. The pollution indices (C_d, HEI and HPI) for heavy metal contamination narrate a different story and indicate heavy metal pollution in the GW at these sites. Therefore, to ascertain true GW-quality at sites wherein both industry and agriculture equally contribute the inclusion of heavy metal pollution indices (C_d, HEI and HPI) in addition to WQI is essential.

Keywords: *Contamination Index, Groundwater, Heavy metal evaluation index, Heavy metal pollution index, Thermal Power Plant*

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INTRODUCTION

Increasing energy demand, agriculture and changing lifestyles, essentially bear a pivotal role of water in supporting the existence of human civilization [1, 2]. This makes it necessary to understand the status quality of GW in quantifiable terms. Extensive researchers and regulatory bodies, have given considerable attention to standardize reference values for important parameters of GW quality [3]. Residents near a thermal power plant (TPP) have primary concern for the quality of water, food, or environment [4]. The adjoining areas of TPPs are reported as containment zone for heavy metals (HMs) like Lead (Pb), Manganese (Mn), Chromium (Cr) and Iron (Fe) which affect the GW quality causing health threats in children [5]. HMs exists as cations or anions eg. Arsenic exists as oxyanions, as colloidal dispersions and suspended particulates and ultimately sink in the aquatic environment. HMs in GW is reported due to weathering of minerals, leaching processes and anthropogenic activities as mining, industrial/domestic effluent or landfill leachate [6, 7]. Modern agricultural activities and industries may release large amounts of HMs which even in small concentrations, affect the quality of water and thereby affect human health [8]. Anpara and Renusagar TPP in Uttar Pradesh are reported to have high concentration of Cd, Ni, Pb and As in water from handpump in post-monsoon season [9]. Singh et al. (1995) documented the concentration of Mn, Fe, Pb, Cu, Cd, Nickel (Ni), Zinc (Zn) in Singrauli region and reported presence of these elements to be maximum at sites closer to TPP's [10]. High concentrations of Fe, Pb, Mn, Cu, Cd are reported in irrigation and drinking water systems discharged from Barapukuria coal mines in Bangladesh [6]. Similarly high concentration of Cr and Pb are reported in Tons and Giri river in the Sirmour district of Himachal Pradesh that pass-through limestone mining belt, receiving runoff water from them. Leaching of As from coal fly ash by rainwater has been reported by several researchers [11, 12]. As, Cd, Pb and other HMs contaminate both soil and GW causing alarm for public health they require strategies for mitigation [9, 13]. It is the direct ingestion or skin intake through which HMs enter the human system [14]. In India, the TPPs are mostly located in peri-urban areas wherein industry and agriculture co-exist. Therefore, the present study aims to assess the comprehensive ground water quality, source of HMs and the pollution degree in vicinity of coal based Thermal Power Plant at Gautam Buddha Nagar in India.

MATERIAL AND METHODS

Site location

Study area is in District Gautam Buddha Nagar, Dadri (28.550°N 77.553°E) Thermal Power Plant (Fig. 1) in the, western Uttar Pradesh, India. It belongs to a warm humid monsoon climate-zone with four distinct seasons, sufficient sunshine and rainfall. The water source for the coal-based thermal power station is the Upper Ganga Canal. This power plant supplies electricity to Delhi and several parts of Uttar Pradesh.

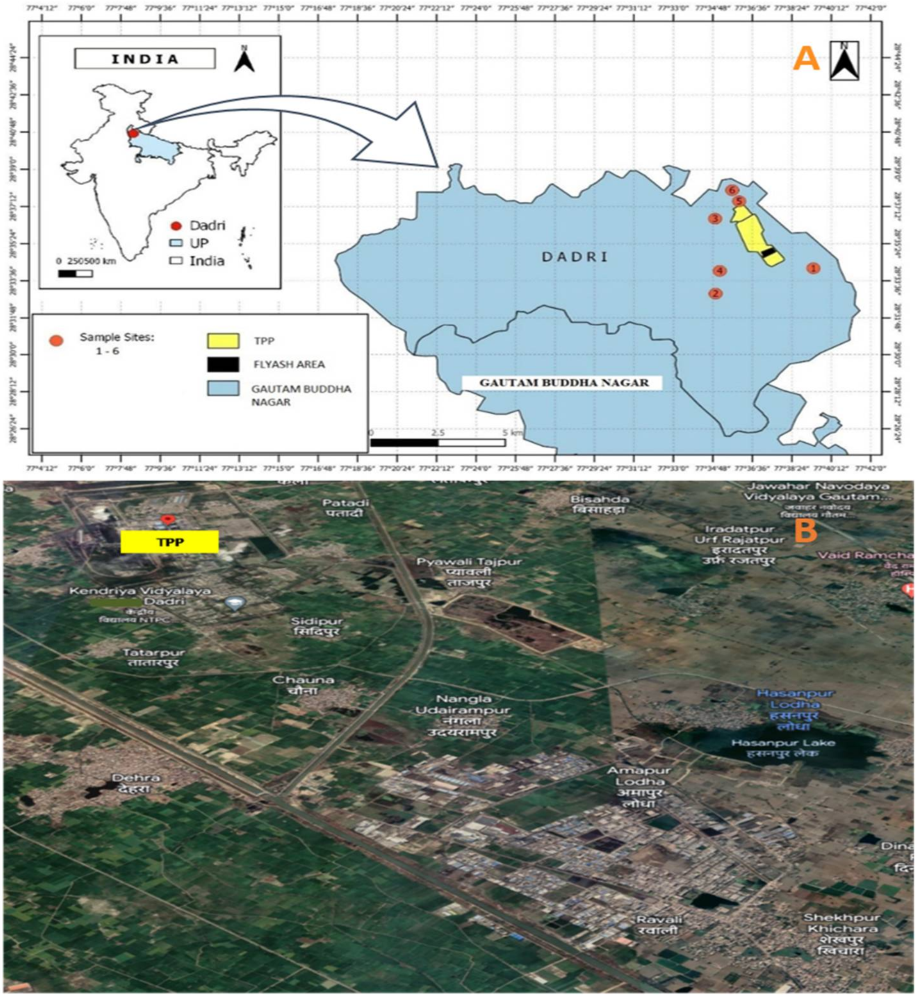

Fig. 1 A (Upper panel) Study area and location of sites near TPP developed using QGIS Geographic Information System Desktop 3.16.16 software [15]. B (Lower panel) Google Earth Image dt. 23.06.2023 showing peri-urban area near TPP [16].

Collection of water samples and analysis of physico-chemical properties

The water samples were collected by random sampling technique from a total of six sites lying within 0-5 km from the TPP. Why were the locations chosen? The samples were collected thrice a year (in triplicate) during post-monsoon (October to January), pre-monsoon (February to May) and monsoon (June to September) seasons for two consecutive years 2017-19. The GW samples were collected from the bore-wells and hand-pumps installed at 250-300 ft. below the surface and stored in separate labelled PTFE containers as per guidelines of American Public Health Association (APHA) manual [17]. Thus, a total of 108 water samples were collected and analysed each year for physico-chemical properties *viz.* pH, Specific

Conductivity, Total Dissolved Solids (TDS), Total Alkalinity as Calcium carbonate, Total Hardness, Biological Oxygen Demand (BOD), Nitrate, Chemical Oxygen Demand (COD), Sulphate, Turbidity, Total Coliform using standard protocols [17] (Table 1). The temperature of water was measured on spot using thermometer and pH of water was measured immediately after collection using multiparameter digital meter (Jenway pH/mV/Temperature meter; Model 3510). Unless otherwise stated the Bureau of Indian Standards (BIS) for drinking water is considered as standard reference [18]. The farmers in the locality were interviewed to substantiate the obtained data for water quality in the area.

Table 1 The groundwater sample analysis of water related parameters carried out using the standard procedures as given in American Public Health Association (APHA) manual and Bureau of Indian Standards (BIS) for drinking water [17, 18].

Sr. No.	Parameters	Unit	Method of analysis	Acceptable Limit	Permissible Limit
1.	pH	1-14	Electrometric Method	6.5-8.5	No Relaxation
2.	Specific Conductivity	µS/cm		–	–
3.	Total Dissolved Solids	mg/l		500	2000
4.	Total Alkalinity as Ca carbonate		Titration Method, APHA (2017)	200	600
5.	Total Hardness		EDTA Titrimetric Method	200	600
6.	Biological Oxygen Demand		5-Day BOD Test, APHA, 2012	–	–
7.	Calcium		EDTA titrimetric method (APHA, 2017)	75	200
8.	Magnesium		Atomic Absorption Spectrometric Absorption, (APHA, 2012)	30	100
9.	Chloride		Argentometric method (APHA, 2012)	250	1000
10.	Fluoride		SPADNS colorimetric method (APHA, 2017)	1.0	1.5
11.	Nitrate		Spectrophotometric method (APHA, 2017)	45	No Relaxation
12.	Chemical Oxygen Demand		Open Reflux Method (APHA, 2017)	–	–
13.	Sulphate		Turbidimetric method (IS 3025, 1986)	200	400
14.	Zinc		Atomic Absorption Spectrophotometer (APHA 2012)	5	15
15.	Arsenic			0.01	0.05
16.	Cadmium			0.003	No Relaxation
17.	Lead			0.01	No Relaxation
18.	Chromium			0.05	No Relaxation
19.	Copper			0.05	1.5
20.	Oil and grease		Partition Gravimetric Method	_	_
21.	Turbidity	NTU	Nephelometric method (APHA, 2012)	1	5
22.	E. coli	MNP/100ml	Multiple tube fermentation technique (MTF) (APHA, 2012)	–	–

Measurement and Calculation of water quality and pollution indices of Heavy Metals (HMs) in water samples

The different HMs (Fe, Zn, As, Cu. Cd, Cr, Pb) were measured in the water samples using Atomic Absorption Spectrophotometer (AAS) following APHA (2012) [17] (Table 1). The data obtained was further used for calculating Water quality index (WQI), Contamination Index (C_d), Heavy Metal Evaluation Index (HEI) and

Heavy Metal Pollution Index (HPI). For calculation of all indices, BIS (2012) standards for drinking water were used [18].

The Water Quality Index (WQI)

WQI was calculated using measured values for physico-chemical parameters of water taking BIS (2012) [18]. The water quality index were calculated as given by Brown et al. (1972) and modified by Tyagi et al. (2013) [19, 20]-

$$WQI = \sum_{i=1}^{n} \mathrm{WiQi}$$

where, Wi is the weight associated with i^{th} water quality parameter, Qi is the sub-index for the i^{th} water quality parameter, and n is the number of water quality parameters. WQI (0-25) is Excellent, WQI (26-50) is Good, WQI (51-75) is Poor, WQI (76-100) is Very Poor, and WQI (> 100) is considered as Unfit for Consumption.

The Contamination Index (C_d)

The degree of contamination of HMs in the GW was evaluated as the Contamination Index (Cd) using the formula given by Backman et al. (1998) [21]-

$$C_d = \sum_{i=1}^{n} C_{fi} \qquad \text{where,} \qquad C_{fi} = C_{Ai}/C_{Ni} - 1$$

The C_d value is calculated as submission of contamination factors of individual component exceeding the upper admissible value. C_{fi}, C_{Ai} and C_{Ni} denote contamination factor, analytical value and upper admissible concentration of the i^{th} component, respectively. N denotes the 'normative value' and C_{Ni} is taken as Maximum Admissible Concentration (MAC).

Heavy Metal Evaluation Index (HEI)

Quality of water in terms of HM might give a complex dataset. The heavy metal evaluation index (HEI) was calculated using formula given by Edet and Offiong (2002) [22]- $\mathrm{HEI} = \sum_{i=1}^{n} \left(\frac{\mathrm{Hc}}{\mathrm{Hmac}}\right)$

Where, Hc is the monitored value of i^{th} parameter and Hmac is the Maximum Admissible Concentration (MAC) of the i^{th} parameter.

Heavy Metal Pollution Index (HPI)

HPI represents the total quality of water with respect to HMs.

$$\mathrm{HPI} = \frac{\sum_{i=1}^{n} \mathrm{WiQi}}{\sum_{i=1}^{n} \mathrm{Wi}} \quad \text{where} \qquad \mathrm{Qi} = \sum_{i=1}^{n} \frac{\{\mathrm{Mi} - (\mathrm{Ii})\}}{(\mathrm{Si} - \mathrm{Ii})} \times 100$$

In the formula, unit weightage of the i^{th} parameter is denoted as Wi, Qi is the sub-index of the parameter, Mi is the monitored value of HM of the i^{th} parameter, Si is the standard permissible value of the i^{th} parameter and n is the number of parameters considered. The Wi is taken as the inverse of the Maximum Admissible Concentration (MAC) as given by Prasad and Bose (2001) [23].

Statistical Analysis

All the tests were performed in three independent replicates. The obtained data were tested using two-way ANOVA with, mean considered significant at $P \leq 0.01$ emphasizing the evidentiary strength of the sample to conclude with confidence that the effect exits.

RESULTS AND DISCUSSION

Table 2 lists the physico-chemical parameters of the water samples collected from test sites during pre-monsoon, monsoon and post monsoon periods.

All the collected water samples were colourless, transparent, odourless and had no significant change in taste. Negligible turbidity of less than 1 NTU was found in all the samples. Oil and grease were absent. The pH, total hardness and TDS for GW samples were in range 6.5-7.8, 187-1736 mg/l and 222-468 mg/l, respectively which were within the Maximum Permissible Limits (MPL) of the BIS (2012) drinking water quality standards (Table 2) [18].

Table 2 Physico-chemical parameters of groundwater for the water samples from the six sites near the thermal power plant at Dadri in 2017-18 and 2018-19 for Pre-monsoon, Monsoon and Post-monsoon periods.

Site	Period	pH	TDS (mg/l)	Total Alkalinity (mg/l)	Total Hardness (mg/l)	COD (mg/l)	BOD (mg/l)	Sulphate (mg/l)	Nitrate (mg/l)	Specific Conductivity (µs/cm)	Total Coliform* (MPN/100ml)	WQI
1	Pre monsoon 2017-18	7.63±0.19	369.00±3.61	175.00±5.00	222.33±5.03	63.33±3.51	2.10±0.20	60.77±0.05	19.65±0.03	394.33±4.04	4.00±1.00	23.59
2		7.67±0.15	393.00±5.00	371.67±3.06	235.00±5.00	31.00±4.00	2.60±0.17	33.54±0.10	18.57±0.21	665.00±5.00	4.67±1.53	25.75
3		7.53±0.13	390.00±5.00	165.67±4.04	332.67±5.03	67.67±4.51	2.20±0.24	89.69±0.06	171.62±0.06	715.00±5.00	4.00±1.00	31.01
4		7.39±0.01	340.00±5.00	365.00±5.00	332.67±5.03	29.33±4.04	2.10±0.30	20.42±0.03	8.91±0.11	675.00±5.00	4.33±1.16	20.93
5		7.63±0.21	340.00±5.00	314.33±4.04	279.67±4.51	13.00±4.00	2.60±0.24	42.74±0.06	10.55±0.15	504.33±4.51	4.00±1.00	23.76
6		7.37±0.07	1467.00±4.58	703.67±6.66	338.67±5.51	52.00±1.73	2.20±0.20	182.67±1.33	143.00±3.00	2871.33±1.16	4.33±0.58	28.64
1	Monsoon 2017-18	7.70±0.19	363.67±4.16	168.00±19.98	240.33±2.08	73.67±3.06	1.5±0.4	64.45±2.98	22.83±1.50	562.33±13.21	6.33±1.53	22.65
2		7.47±0.35	422±13.08	439.33±10.26	257.67±34.39	35.00±2.65	1.7±0.1	35.33±3.51	34.68±3.51	756.67±9.29	5.67±1.16	20.18
3		7.33±0.49	428±10.58	178.67±5.51	358.67±17.39	39.52±4.50	1.9±0.2	89.51±1.00	159.78±6.74	835.33±11.15	5.67±1.53	25.48
4		7.26±0.11	376.00±13.00	362.00±11.36	267.67±10.97	49.33±1.53	1.7±0	22.56±1.97	9.18±0.63	759.00±199.03	5.33±0.58	20.21
5		7.43±0.39	369.00±19.70	363.00±19.31	269.00±28.62	37.00±5.57	1.6±0.3	53.51±1.53	12.94±1.55	538.67±62.52	5.00±2.00	19.81
6		7.28±0.32	1736.67±99.20	952.67±26.73	329.33±16.62	68.00±4.36	1.5±0.4	227.06±6.95	131.47±6.33	3360.67±244.36	4.00±1.00	26.19
1	Post-monsoon 2017-18	7.78±0.27	366.00±15.62	180.00±6.93	222.33±1.53	76.00±5.00	2.20±0.24	60.93±0.57	22.88±3.40	513.67±105.57	6.00±1.00	27.24
2		7.62±0.33	396.67±20.53	402.67±25.00	264.67±22.37	39.67±4.73	2.10±0.70	55.20±11.60	10.89±1.42	549.33±38.55	6.67±1.53	24.09
3		7.76±0.24	400.67±44.06	182.67±7.10	298.33±105.67	51.67±21.96	2.30±0.40	91.21±1.36	161.49±8.78	783.00±56.24	7.00±1.00	30.81
4		7.58±0.25	364.33±30.09	342.67±30.09	288.67±47.29	39.00±3.61	2.40±0.10	24.93±8.49	7.87±0.94	549.67±180.11	5.33±1.53	24.70
5		7.50±0.27	366.33±24.21	341.00±19.52	287.67±1.52	27.67±4.51	2.00±0.40	55.20±11.60	10.89±1.42	549.33±38.55	4.67±0.58	21.62
6		7.54±0.28	1507.67±161.48	834.00±108.57	359.33±54.85	61.00±5.57	2.60±0.10	199.01±11.53	144.58±14.16	3255.00±425.4	3.67±2.08	33.57
1	Pre-Monsoon 2018-19	7.40±0.10	187.00±244.26	278.67±10.02	282.67±3.06	46.33±3.06	2.50±0.50	63.24±0.02	25.33±0.01	976.33±2.31	8.33±0.58	24.78
2		7.33±0.15	463.33±2.89	420.67±0.58	281.00±3.61	47.67±1.53	2.10±0.20	35.67±0.00	3.02±0.01	1027±5.13	6.33±2.08	22.26
3		7.37±0.15	545.00±1.00	265.00±1.00	442.67±2.52	35.67±8.15	2.60±0.40	81.15±0.00	2.65±0.02	966.00±2.00	5.67±1.53	25.99
4		7.63±0.25	531.33±20.31	462.00±2.65	332.67±6.81	48.67±0.58	2.70±0.20	26.27±0.15	4.61±0.17	1041.00±3.61	6.67±2.08	28.02
5		7.47±0.15	463.33±4.93	358.33±2.08	245.33±0.58	37.33±4.04	2.60±0.20	58.25±0.001	11.43±0.01	992.33±5.13	7.00±1.73	26.76
6		7.47±0.23	1428.00±1.00	678.33±2.52	468.00±3.00	50.00±5.57	2.40±0.40	273.00±4.36	14.23±0.02	1505.33±3.22	8.00±1.73	27.08
1	Monsoon 2018-19	7.37±0.15	1062±6.56	720.33±3.056	349.43±0.57	45.33±0.58	2.20±0.24	231.00±4.58	62.33±1.53	2879.33±4.51	8.67±0.58	23.59
2		6.97±0.12	1072.33±23.46	819.33±8.08	264.00±7.00	45.67±0.57	1.80±0.70	142.64±0.02	54.33±1.53	2132.67±9.82	6.67±0.58	21.41
3		6.47±0.15	355.33±3.51	344.67±4.04	268.67±2.08	46.33±2.31	1.60±0.40	78.67±1.07	8.90±0.11	1024.33±4.04	7.33±0.58	15.86
4		7.40±0.17	638.67±4.16	177.33±2.08	250.00±3.46	51.33±2.52	1.80±0.10	58.20±0.00	23.00±0.17	973.00±7.21	6.00±1.00	21.21
5		7.50±0.10	915.67±3.51	324.33±4.04	277.00±5.57	45.33±1.53	1.50±0.40	130.32±1.50	21.89±0.02	1417.06±7.98	9.00±1.00	20.26
6		7.47±0.15	926.33±5.69	419.67±5.03	439.33±1.53	36.00±1.00	1.90±0.10	164.33±0.58	0.63±0.00	1180.00±2.00	8.33±0.58	22.61
1	Post-monsoon 2018-19	7.30±0.17	470.33±5.77	292.00±5.20	284.33±0.58	54.67±0.58	2.2±0.3	62.56±1.16	25.65±0.58	967.33±11.55	7.33±0.58	23.43
2		7.47±0.12	468.00±0.00	425.00±0.00	284.00±0.00	36.00±0.00	2.4±0.2	36±0	3.02±0	1025±0	6.33±0.58	23.62
3		7.23±0.12	536.67±5.77	253.33±11.55	435.67±5.77	31.00±0.00	2.5±0.1	80.79±0.58	2.61±0.06	931.67±57.74	4.67±1.16	24.38
4		7.50±0.17	506.67±4.62	460.33±4.04	333.67±15.01	61.67±0.58	2.1±0.1	26.32±0.02	4.53±0.02	1031.67±5.77	6.67±0.58	24.93
5		7.27±0.06	469.33±7.51	360.33±7.51	248.33±5.77	31.13±1.62	2.2±0.2	57.38±1.5	11.37±0.1	985.73±17.78	6.67±0.58	22.95
6		7.43±0.58	1431.67±11.55	678.00±0.00	451.67±23.1	63.67±0.58	2.4±0.2	284.67±11.55	14.23±0	1539.33±57.74	6.33±0.58	28.02

*No *E. coli* could be determined in any of the water samples during the study. Agreeable odour and taste was noted for all water samples. All the water samples were colourless and transparent.

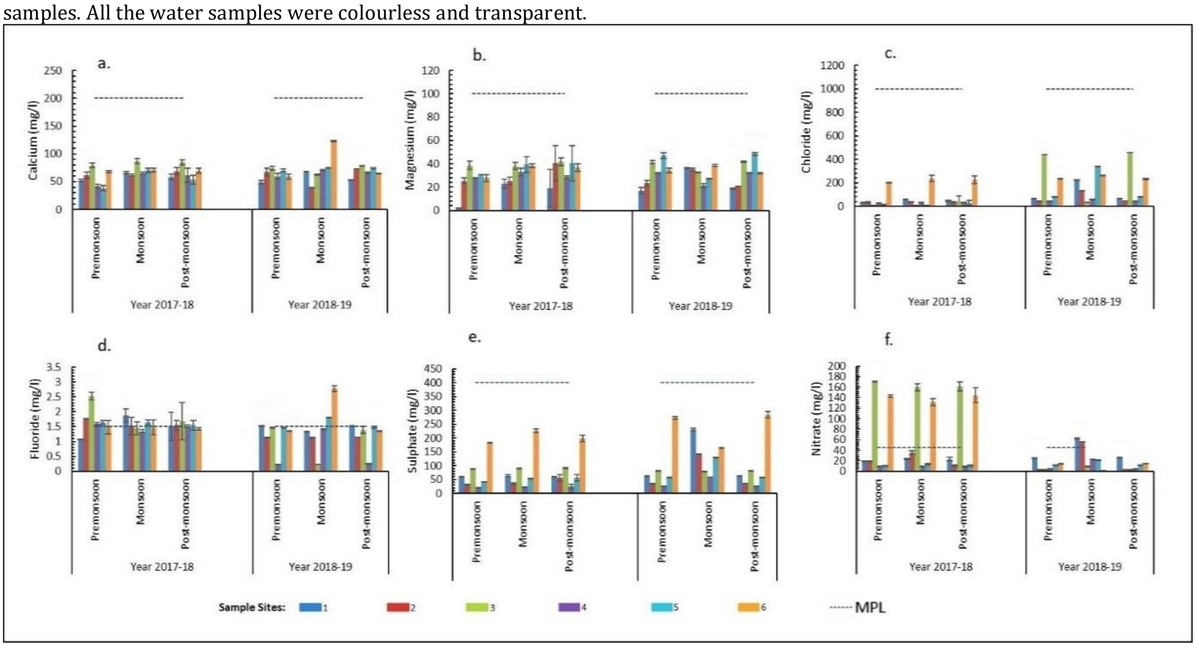

Fig. 2 Levels of different ions in mg/l in the water samples from six sites near the thermal power plant at Dadri in 2017-18 and 2018-19 during pre-monsoon, monsoon and post-monsoon periods. a. calcium; b. magnesium; c. chloride; d. fluoride; e. sulphate and f. nitrate. Values are mean of three replicates ±SD.MPL: Maximum Permissible Limit of ions in drinking water as per BIS (2012) standards [18].

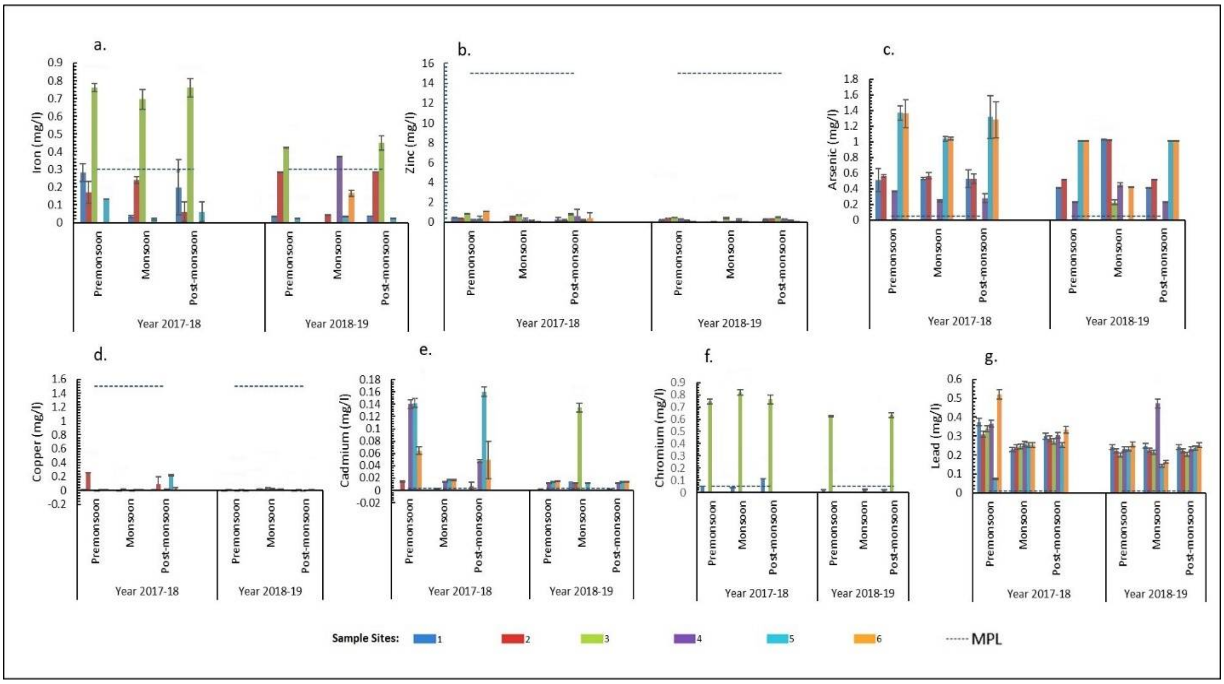

Fig. 3 Levels of different heavy metal ions in mg/l in the water samples from six sites near the thermal power plant at Dadri in 2017-18 and 2018-19 during pre-monsoon, monsoon and post-monsoon periods. a. iron; b. zinc; c. arsenic; d. copper; e. cadmium; f. chromium and g.lead. Values are mean of three replicates ±SD. MPL: Maximum Permissible Limit of the ions in drinking water as per BIS (2012) standards [18].

The water appeared to be slightly basic and hard which is also supported by the presence of high amount of calcium (Fig. 2a), magnesium (Fig. 2b) and iron (Fig. 3a) in water from the test sites. The EC of 2879.33 and 2132.67 µs/cm and total alkalinity of 720.3 and 819.3 mg/l were noted at site-1 and site-2 during monsoon of 2018-19 which exceeded MPL. Jameel and Sirajuddin (2006) suggested EC and alkalinity to be a result of increased percolation rate of industrial effluent, domestic waste and agricultural waste bearing high load of dissolved solids. BOD of water was >3 in all seasons [24]. Maximum COD of 76 mg/l was noted at site-1 in 2017-18, and site-4 (68.67 mg/l) in 2018-19, during post monsoon period, respectively. The increase in COD in water is indicative of the contribution of inorganic material susceptible to oxidation by oxidants largely present in industrial effluent at sites near the TPP. Absence of *E. coli* in all the water samples suggested no faecal contamination at any of the studied sites.

The mean Water Quality Index (WQI) obtained for pre monsoon, monsoon and post-monsoon periods (Table 2) suggest the quality of GW prevailing at these sites to be good and adequate throughout the year. The WQI for the six sites near TPP suggest altered water quality with monsoons which dilutes the levels of salt, TDS, turbidity and specific conductivity due to rainfall.

Fig. 2 (a, b, c, d, e and f) represents the levels of different ions namely Calcium (Ca), Magnesium (Mg), Chloride (Cl^-), Fluoride (F^-), Sulphate (SO_4^{2-}) and Nitrate (NO_3^-), respectively. The concentration of different HMs including Fe, Zn, As, Cu, Cd, Cr and Pb is represented as (Fig. 3a, b, c, d, e, f and g), respectively. Ca, Mg and Zn are present in GW naturally due to properties of parent rock material of the zone. Ca (Fig. 2a) and Mg (Fig. 2b), were found to be within the MPL of drinking water quality standards. Chou et al. (1989) suggested that solubility of these metal ions is controlled by pH and dissolved CO_2 as these form Calcium carbonate (Calcite) and Calcium magnesium carbonate (Dolomite) [25]. In this study, the formation of calcium salts above could be a consequence of both timing and chemistry of water or metal ion conditions or due to geological activities in the region. The calcium rich carbonate as as calcite and dolomite are abundant on earth. The atmospheric CO_2 produces carbonate rock through aqueous chemical weathering contributing towards surficial carbon. The small proportion of primary magnesium carbonate is a consequence of weathering of Ca dominant silicates rocks and pre-existing carbonate rocks [26]. Though within the admissible limits, the level of copper in GW of site-2 were significantly higher throughout the study period as compared to other sites. $Cl^-$and SO_4^{2-} concentrations (Fig. 2c and 2e, respectively) in the water for all the sites were also within the maximum permissible limits of the Indian Standards. Owing to geographical location of Dadri that falls in the fluoride belt [27], the level of F (Fig. 2d) was much higher in the GW of site-1, site-2 and site-3 as compared to other sites. Elevated nitrate levels in water bodies of developing nations has been directly linked to more consumption of pesticides and N-fertilizer for agriculture that leaches and contaminates the GW bodies [28]. The nitrate concentration (Fig. 2f) was noted to be significantly high at site-3 (171.62, 159.78 and 161.49 mg/l) followed by that at site-6 (143, 131.47 and 144.58 mg/l) during pre-, monsoon and post-monsoon seasons, respectively for the year 2017-18 (Table 2). Use of large volume of fertilizers by the farmers in the Dadri region was also affirmed from the interviews with the farmer's onsite suggestive of considerably high inputs of nitrate from agricultural runoff in GW. Moreover, it is also likely that excess rainfall or irrigation results in water movement in the soil through deep percolation carrying with it soluble nutrients, particularly nitrate and sulphate.

Except for site-6 the WQI values calculated for quality of water at the six sites reflect good drinking water quality standard. Site-6 is located at the T-junction of Upper Ganga Canal where it bifurcates and moves down-South and is likely to contribute towards the water quality of GW aquifers affecting thereby the water quality at this site, however this needs further confirmation. Enrichments in the heavy metal in the GW can also be attributed to activities and waste products washed by surface runoff into the feeder canals near the TPP [22]. The agricultural runoff therefore may be contributing to alterations in quality of canal water being used for irrigation in this study. Though Dadri region is an established fluoride belt due to natural geochemical cycle [27] and in general fluoride levels are high in the GW, however, interviews with the farmers did not reveal any case of fluorosis either current or in the previous years at any of the sites in this study.

Levels of different HMs in the GW samples from all six sites near TPP (Fig. 3) suggest Fe level to be 0.22 mg/l at site-2, whereas highest level of Fe beyond the BIS (2012) limit (0.3 mg/l) was recorded at site-3, i.e. 0.40 mg/l. All the other sites had Fe concentrations in GW to be within the standard limits (Fig.3a). Among all the sites, site-3 had the maximum level of Zn (0.94 mg/l) in its GW samples (Fig. 3b). Variations in As due to change in seasons were noted in this study as also reported by Sobhanardakani et al. (2017) in studies carried out at Toyserkan Plain in Iran [29]. The As values were significantly above the acceptable limits in GW samples (MPL for As in GW is 0.05 mg/l) [18] at site-5 and site-6 compared to other sampling sites (Fig 3c). Contribution of precipitation during monsoon leading to dilution of As in GW samples is evident (Fig 3c). The HMs ingested by animals and human accumulate in the kidneys, where it may result in the organ dysfunction [30] and therefore are of concern in GW [5]. Inorganic As is a confirmed carcinogen and most significant chemical contaminant in drinking-water however, no immediate symptoms of any arsenic poisoning were reported by the villagers within study area. The Cu levels were within the MPL of 1.5 mg/l of Indian standards. Low Cu levels were noted at all the sites during the study except site-2 in pre-monsoon period and site-5 in post-monsoon where slightly elevated levels of Cu were noted i.e., 0.24 and 0.22 mg/l respectively during 2017-18 (Fig. 3). It is unsure why this elevation in Cu levels occur but the most likely cause is the leaching of accumulated Cu from various sources including pesticides, drains, and effluent from TPP or contributed by hydrogeological processes into the GW during pre-monsoon period. Further, site-3 having high Fe and low Cu levels also suggest chelation of Cu in presence of elevated Fe limiting its leaching to the GW. Concentrations of Cd were high at site-2, site-4, site-5 and site-6 throughout the year however, a 50 times higher Cd was recorded in the GW samples from site-3 during pre-monsoon period (Fig. 3). Cr being a crucial HM for human life is given no relaxation beyond the acceptable limit of 0.05 mg/L as per the drinking water standards. Its significant presence at site-3 throughout the sampling period suggests release of Cr in GW (Fig. 3f). The input of Cd/ Cr in GW could perhaps be due to agricultural runoffs, leaching from nearby landfills or dumping sites or from coal-burning causing fly ash deposition [12], on the surface of water bodies or due to major geochemical process in that belt [31]. The consumption of water containing high level of Cd/Cr could result in health problems [32]. Fly ash is reported by researchers to be the main reason for the higher concentrations of Pb, Cd, Ni and As near TPPs [9, 12]. Exposure to high levels of Pb causes brain and central nervous system dysfunction causing coma, convulsions and even death. The concentrations of 30.95 to 59.00 µg/g and 47.05 to 89.90 µg/g of Pb is reported in Indian coal used in TPP and the corresponding fly ash, respectively [33]. The levels of Pb were 15-20 times higher in the GW samples at all sites exceeding MPL of 0.01 mg/l (Fig. 3g), suggesting leaching of Pb from the ash cooling ponds. The accumulation of Pb in GW could also be due to the sanitary landfills in the nearby areas however, a detailed source apportionment study is required for better understanding.

A closer investigation revealed that the monsoon of 2018 experienced about 115% more rainfall (~459mm) when compared to monsoon of 2017 (~213 mm). Along with the rainfall runoff, the air pollutants from urban surface are also released into water bodies [34]. The lowering of Fe, Cr, As and Mg levels in monsoons is due to dilution and therefore, their input in GW might not be from the parent rock material, but from the coal combustion residues.

Table 3 Inputs and computed pollution indices Contamination Index (C_d), Heavy Metal Evaluation Index (HEI) and Heavy Metal Pollution Index (HPI) in groundwater samples from the area of study.

Sample Site	Heavy Metals	Standard Permissible Limit (Si)	Ideal Value (Ii)	Monitored Value (C_{Ai} or H_c or M_i)	Maximum Admissible Conc.(MAC) or C_{Ni} or H_{mac}	Contamination Factor for the ith component (C_{fi}= C_{Ai}/C_{Ni}-1)*	Contamination Index $C_d=\sum_{i=1}^{n} C_{fi}$	Mean HEI	Unit Weight Value (Wi or 1/ H_{mac})	Qi= |Mi-Ii|/(Si-Ii)*100	WiQi	HPI	Overall HPI $=\frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi}$
1.	**Iron (Fe)**	300	0	50	200	-0.7500	8.7441	51.40	0.005	16.6667	0.0833	0.0797	205.8606
	Zinc (Zn)	15000	5000	102.9	5000	-0.9794			0.0002	48.971	0.0098	0.0094	
	Arsenic (As)	50	10	571.7	50	10.4340			0.02	1404.25	28.085	26.844	
	Copper (Cu)	1500	50	6.5	1000	-0.9935			0.001	3	0.003	0.0029	
	Cadmium (Cd)	3	0	5.1	3	0.7000			0.3333	170	56.67	54.164	
	Chromium (Cr)	50	0	24.2	50	-0.5160			0.02	48.4	0.968	0.9253	
	Lead (Pb)	100	10	184.9	1.5	0.8490			0.6667	194.33	129.56	123.834	
2.	**Iron (Fe)**	300	0	215.8	200	0.0790	11.0567	47.93	0.005	71.93	0.3597	0.3438	210.2759
	Zinc (Zn)	15000	5000	305.4	5000	-0.9389			0.0002	46.95	0.0094	0.009	
	Arsenic (As)	50	10	625.4	50	11.5080			0.02	1538.5	30.77	29.411	
	Copper (Cu)	1500	50	14.6	1000	-0.9854			0.001	2.44	0.0024	0.0023	
	Cadmium (Cd)	3	0	5.1	3	0.7000			0.3333	170	56.6667	54.164	
	Chromium (Cr)	50	0	41.6	50	-0.1680			0.02	83.2	1.664	1.5905	
	Lead (Pb)	100	10	186.2	1.5	0.8620			0.6667	195.78	130.52	124.75	
3.	**Iron (Fe)**	300	0	401.8	200	1.0090	15.2940	60.56	0.005	133.933	0.6697	0.6401	338.1659
	Zinc (Zn)	15000	5000	939.2	5000	-0.8122			0.0002	40.608	0.0081	0.0078	
	Arsenic (As)	50	10	61	50	0.2200			0.02	127.5	2.55	2.4374	
	Copper (Cu)	1500	50	16.8	1000	-0.9832			0.001	2.2897	0.0023	0.0022	
	Cadmium (Cd)	3	0	19.6	3	5.5333			0.3333	653.33	217.78	208.16	
	Chromium (Cr)	50	0	536.2	50	9.7240			0.02	1072.4	21.448	20.501	
	Lead (Pb)	100	10	160.3	1.5	0.6030			0.6667	167	111.33	106.42	
4.	**Iron (Fe)**	300	0	82.8	200	-0.5860	5.2777	64.12	0.005	27.6	0.138	0.1319	261.6582
	Zinc (Zn)	15000	5000	251.4	5000	-0.9497			0.0002	47.486	0.0095	0.0091	
	Arsenic (As)	50	10	281.2	50	4.6240			0.02	678	13.56	12.961	
	Copper (Cu)	1500	50	7.8	1000	-0.9922			0.001	2.9103	0.0029	0.0028	
	Cadmium (Cd)	3	0	9.8	3	2.2667			0.3333	326.67	108.89	104.08	
	Chromium (Cr)	50	0	39.8	50	-0.2040			0.02	79.6	1.592	1.5217	
	Lead (Pb)	100	10	211.9	1.5	1.1190			0.6667	224.33	149.56	142.95	
5.	**Iron (Fe)**	300	0	43.7	200	-0.7815	16.3798	83.04	0.005	14.5667	0.0728	0.0696	282.0504
	Zinc (Zn)	15000	5000	203.1	5000	-0.9594			0.0002	47.969	0.0096	0.0092	
	Arsenic (As)	50	10	853.8	50	16.0760			0.02	2109.5	42.19	40.327	
	Copper (Cu)	1500	50	12.3	1000	-0.9877			0.001	2.6	0.0026	0.0025	
	Cadmium (Cd)	3	0	11.8	3	2.9333			0.3333	393.33	131.11	125.32	
	Chromium (Cr)	50	0	18.3	50	-0.6340			0.02	36.6	0.7320	0.6997	
	Lead (Pb)	100	10	173.3	1.5	0.7330			0.6667	181.44	120.963	115.62	
6.	**Iron (Fe)**	300	0	58.1	200	-0.7095	20.2177	74.18	0.005	19.3667	0.0968	0.0926	315.7825
	Zinc (Zn)	15000	5000	126.5	5000	-0.9747			0.0002	48.735	0.0097	0.0093	
	Arsenic (As)	50	10	1022.1	50	19.4420			0.02	2530.25	50.605	48.37	
	Copper (Cu)	1500	50	8.2	1000	-0.9918			0.001	2.8828	0.0029	0.0028	
	Cadmium (Cd)	3	0	12.8	3	3.2667			0.3333	426.667	142.22	135.94	
	Chromium (Cr)	50	0	11.8	50	-0.7640			0.02	23.6	0.472	0.4512	
	Lead (Pb)	100	10	194.9	1.5	0.9490			0.6667	205.4444	136.963	130.91	

Table 3 lists the input and the site-wise computed pollution indices including Contamination Index (C_d), Heavy Metal Evaluation Index (HEI) and Heavy Metal Pollution Index (HPI) in GW samples in the study area for individual heavy metals. Table 4 represents the overall GW quality near TPP based on pollution indices classes modified and adopted from various researchers. The C_d values for the studied sites varied in the range of 5.28 (site-4) and 20.22 (site-6) and reflected as 33% low, 50% medium and 17% sites with high contamination (Table 4). The degree of contamination (extent of metal pollution) suggests more contamination of HMs in and around TPP at these sites. Such variations may occur as a consequence of the total number of metal ions considered/tested for calculating C_d, very high concentration of any one or two metal ions, distance and direction from TPP and due to different standard limits for metals accepted from water standards given by different agencies including WHO (2008), EPA (2002) [35, 36]. Of all the indices HEI is preferred as a more reliable assessment method for HM pollution as it provides a better result compared to C_d or HPI. Among all sites, site-2 had lowest HEI value of 47.93 whereas the maximum HEI of

83.04 was noted for site-5 (Table 4). HEI values were categorized in low, medium and high classes (modified and adopted from Edet and Offiong, 2002) [22]. The HEI for almost 33% sites was low, 50% medium and 17% were high (Table 4) indicating the GW at these sites to be contaminated with HMs. The higher HEI values appear to be a consequence of high Pb concentrations at these sites (Fig. 3g) which is much beyond the acceptable limits. Kapoor and Christian (2016) reported an inverse relation between the HM pollution and distance from the point source however, no such correlation could be observed in this work [37]. From the HEI values however, it appears that the quality of GW improved during 2018-19 as compared to 2017-18. Site-4 being the closest (within 0-4 km) to the TPP, its GW appeared to receive a heavier metal load from leaching. The Heavy Metal Pollution Index (HPI) was minimum (205.86) at site-1 and maximum at site-3 (338.17). The HPI predominantly reflects 67% locations falling in medium polluted category while rest 33% were recognized with high HPI indicating the GW in the area to be more polluted with HMs (Table 4).

Table 4 Overall groundwater quality near TPP based on pollution indices classes modified and adopted from [1]Brown et al. (1972), [2]Backman et al. (1998), [3]Edet and Offiong (2002) and [4]Prasad and Bose (2001) [19, 21, 22, 23].

Index Method*	Minimum	Maximum	Mean	Class	Description	No. of Sites	%age of sites
[1]WQI	22.52	27.69	25.11	0-25	Excellent	4	67
				26-50	Good	2	33
				51-75	Poor	-	-
				76-100	Very Poor	-	-
				>100	Unfit for Consumption	-	-
[2]C_d	5.28	20.22	12.75	<10	Low	2	33
				10-20	Medium	3	50
				>20	High	1	17
[3]HEI	47.93	83.04	65.49	<60	Low	2	33
				60-80	Medium	3	50
				>80	High	1	17
[4]HPI	205.86	338.17	272.02	<150	Low	-	-
				150-300	Medium	4	67
				>300	High	2	33

CONCLUSION

In conclusion, the WQI of the GW at Dadri near the TPP reflect seasonal variation and suggests that through the water appears to be fit for domestic use yet this is not true. The pollution indices (C_d and/or HEI and/or HPI) for heavy metal contamination narrate a different story. Therefore, it is not only the physico-chemical parameters of GW and corresponding WQI which is important to ascertain the quality of GW, but also it is more important to include the heavy metal pollution indices (C_d and/or HEI and/or HPI) in a peri-urban area owing to the contribution of both industry and agriculture towards GW quality. This implies that long term utilization of agricultural fertilizers/pesticides, use of waste water and sewage sludge for irrigation and establishment of industries releasing pollutants in the vicinity of agricultural farms threaten the groundwater quality and may cause irreversible damage in the region. Accounting for the proportionate contribution from industrial and agricultural sources needs to be carried out in future. Innovative and efficient technologies are further required along with sustainable measures to address harmony between coal fired thermal power generation plant, environmental pollution and agriculture in the region.

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Author Contribution

Shalini Gupta: Data collection, methodology, Naveen Kumar: manuscript writing, editing, Vyomendra Chaturvedi: manuscript writing, editing, Kavita Shah: Conceptualization, reviewing, editing.

Data availability

This paper includes all the relevant data or supplementary information.

Competing interests

The authors declare that they have no competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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