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Seasonal Variation of Fe, Mn, and Pb in Groundwater of Northwestern Bangladesh

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Abstract

Groundwater is one of the most significant natural resources on earth and also stands as the largest source of all-purpose water in Bangladesh. The higher concentrations of iron (Fe), manganese (Mn), and lead (Pb) in water constitute a threat to human health and the environment. The research aimed to assess the seasonal variations of heavy metal concentrations, including Fe, Mn, and Pb, and the water type controlling the geochemistry of groundwater. A total of sixty groundwater samples were collected over a year in three seasons and analyzed for several physicochemical parameters using the standard analysis methods The highest concentrations of Fe, Mn, and Pb in investigated groundwater samples were found to be 3.69, 2.50, and 0.17 mg/L, respectively. The study observed that the higher concentrations of Fe and Mn were in the pre-monsoon but Pb was in the post-monsoon. The contaminations of Fe, Mn, and Pb in the groundwater follows the order Fe > Mn > Pb in three seasons, and their concentrations of abundance follow the seasons: PRM > POM > MON. The groundwater samples showed the dominance of Ca^{++}, Mg^{++}, and HCO_3^-, indicating temporary hardness and the Ca-Mg-HCO_3, hydrochemical facies, controlling the groundwater geochemistry in the study area. These findings would provide an in-depth understanding of water quality, potential risks to human health, and coping mechanisms for sustainable drinking water management.

Keywords: Contamination, groundwater, seasonal variation, geochemistry, heavy metal,

1. Introduction

In the entire world, groundwater is regarded as one of the most significant natural resources on earth and contains minerals that are tremendously significant in human nutrition [1]. Due to its purity, both urban and rural parts of Bangladesh depend heavily on groundwater as a drinking water source [2]. but the majority of people live in rural areas depend largely on their home and agricultural needs [3]. Till 1997, it has been claimed that 97% of people relied on groundwater as a reliable drinking water source, and 70% of irrigation water comes from groundwater [4]. Though groundwater is one of the most significant water sources for human health [5, 6] the quantity of groundwater is just as important as the quality of the groundwater because the health profile of a community depends on its uses [7]. It's been noticed that more frequent groundwater metal pollution more often than not goes unreported and is concealed from the gaze of the general groundwater have vital functions in the body, but only if their levels stay below a certain range as advised by the World Health Organization [9]. Water normally contains trace levels of metals, which are usually acceptable for human health [10], but elevated levels of contamination are injurious to health and the environment. Various researchers have also shown that trace metals such as Cr, Fe, Mn, Cd and Pb are major toxicants in contaminated water [11, 12, 13, 14, 15, 16]. The Fe, Mn, and Pb concentration in groundwater changed in different seasons. So, groundwater quality changes in different seasons showed seasonal variations, most significantly.There are many factors including agricultural activities, geology, landfill leachate, discharged wastewater, and intrusion of saltwater responsible for the variation of water quality parameters. Heavy metals concentrations including Fe, Mn, and Pb in groundwater were higher in the dry season, while microorganisms were higher in the wet season [17].

Fe and Mn are necessary nutrients for human's health but Pb is a toxic metal (Heavy metal) that is categorized as a priority pollutant by the USEPA. Pb is not require any purpose for human body. The Fe and Mn source in groundwater are geogenic, such as weathering and leaching of Fe and Mn-containing rocks and minerals into the aquifers, but continuously, a large amount of Pb are discharged into the groundwater by human activities [18, 19, 20]. For drinking purposes, the national standard (BDWS and BECR) limits of Fe, Mn, and Pb in groundwater are 0.3-1.0, 0.1, and 0.05 mg/L, respectively [21]. The concentrations of Fe, Mn, and Pb in the groundwater of Bangladesh was higher than the permissible limits of different national and international organizations as the BECR, BDWS, WHO, INDIA, and US-EPA standards in three seasons [21, 22, 23, 24, 25, 26, 27, 28]. Fe, Mn, and Pb exposure is linked to the greatest risks to human health. International organizations like the WHO frequently assess these metals' impacts on human health as a result of substantial research into them [29, 30, 75].

Groundwater quality is also significantly influenced by geomorphology, hydrogeology, and depositional history. The hydro-geochemical research being done in two upazila thus far, meanwhile, is inconsequential. Consequently, a hydrogeochemical analysis has been conducted because of worries about how such factors may affect the utilization of groundwater. These two upazila reveal the number of water-bearing zones in connection to geological structures, the mineral makeup of the sediments in the water-bearing zone, and the chemical makeup of the groundwater in addition to the current subsurface environment at a 50-meter depth. [2]

Through a review the research articles past two decades there were no previous studies to assess the seasonal variation of Fe, Mn, and Pb in the groundwater of this area. However, a small number of studies have measured the vertical distribution of major and trace elements in the aquifers of northwestern Bangladesh. Their research on groundwater focused solely on arsenic, [31, 32, 33, 34, 35] groundwater pollution and health hazard [36]. Thus, this study denoted the concentration level and seasonal variation of Fe, Mn, and Pb in the groundwater of northwestern Bangladesh (Chapi Nawabganj District) for the first time. The objectives of this research were to investigate the collected groundwater from the shallow tubewells of the research area to a) assess the contamination level of Fe, Mn, and Pb, b) determine vertical geochemical variations and seasonal variation of Fe, Mn, and Pb, (c) show correlation between Fe, Mn, and Pb. The results of this study provide decision-makers with an in-depth understanding of water quality, information about potential risks to human health, and illumination of the theoretical foundations of risk-reduction strategies and coping mechanisms for the creation of sustainable drinking water systems.

2. Methods and Materials

2.1. Research area

The research area covers 977.2 km^2 together with Chapai Nawabganj Sadar and Shibganj upazila of Chapai Nawabganj district, northwestern Bangladesh. This region belongs to geographical co-ordinates between 24°24' to 24°55' north latitudes and between 88°10' to 88°26' east longitudes (Fig. 1). It is surrounded by Bholarhat, Gomastapur, Nachole and West Bengal of India in the north, West Bengal of India in the south and west, Tanore and Godagari upazila of Rajshahi district in the east. The Padma is a transboundary river between Bangladesh and India that runs throughout the research area. It is located in the Younger Ganges and older Mahananda floodplain, which has a gentle slope and elevations between 20 and 25 meters above mean sea level, whereas groundwater runs towards the gradients from north to south [31]. This area belongs to a tropical humid-arid climate and is generally characterized by monsoons, high temperatures, high humidity, and moderate rainfall. The research area has a tropical, wet and dry, or savanna climate.

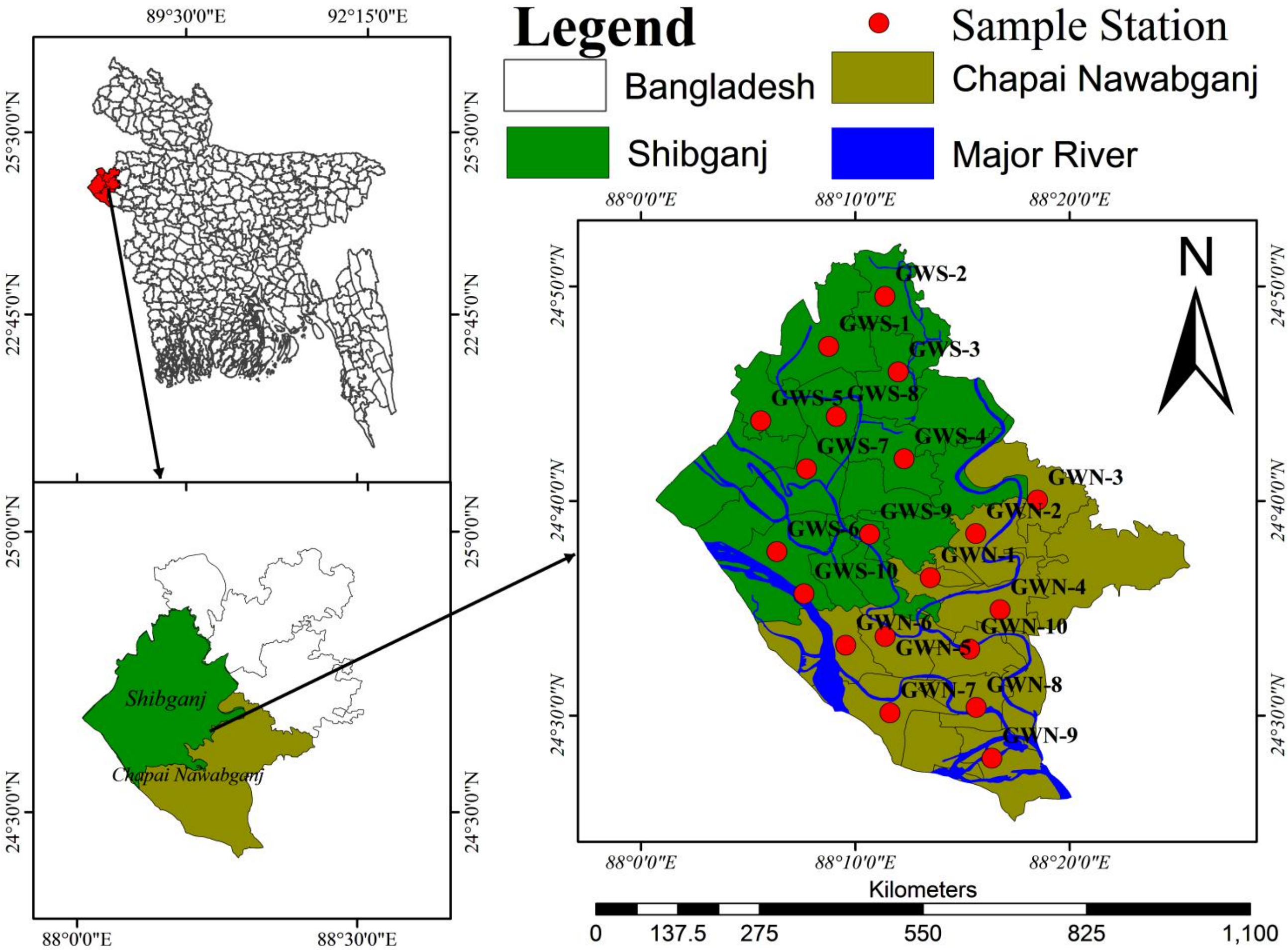

Figure 1. Study Area and sample station of northwestern Bangladesh.

The yearly temperature of this district is 29.4ºC (Max. 37.8 °C in April – Min. 11.2 °C in January) and it is 1.66% higher than the average rainfall of Bangladesh. Monsoon season brings the highest amount of rainfall. Annual rainfall for this area is approximately 1,158 Millimeters (45.59 inches) [37]. There are two distinct geomorphologies in the research area: Barind Tract is in the north-east portion, and the Old Mahananda floodplains and Young Ganges floodplains are in the south-west portion [2]. The Chapai Nawabganj region is composed of alluvial sediments that were laid down by the Ganges and Mahananda Rivers' meandering channels. The underlying sediments of Chapai Nawabganj district are divided into four units such Grey silts and extremely fine-grained sandy overbank floodplain deposits (thickness of 0-45 m), orange-gray hard clays and Barind Tract siltstones that are deposited in a meandering channel system (thickness 45-80 m), sediments of grey brown micaceous that associated silty overbank sediments (thickness 35– 45 m) and the Barind Tract which is consist of silty and orange grey clays [38].

2.2. Groundwater sample collection, preparation, processing and analysis

A total of sixty groundwater samples were collected from the study area for analyzing major cations, anions and trace elements from hand tube well (depth ranges from 30 to 50 m) in three seasons September 2022, February 2023 and May 2023, respectively pre monsoon (PRM), monsoon (MON) and post monsoon (POM). For sample collection, first each tube well pumped about five/six minutes and then collected water samples in two plastic bottles of 500 mL each for anion and cation. Then, add 5 ml conc. HNO_3 (Fluka Analytical, Sigma-Aldrich, Germany) into the indicator bottles were corked instantly and reserved it in an ice box to prevent oxidation.

Table 1. Summary of the physicochemical parameters, major cations-anions and trace elements composition of studied groundwater samples of northwestern Bangladesh.

Parameter	PRM				MON				POMo				WHO Standard
	Min	Max	Average	STD	Min	Max	Average	STD	Min	Max	Average	STD	
pH	7.6	8.5	7.989	0.235	7.1	7.8	7.410	0.189	7.9	9	8.240	0.264	8.5
EC	501	1024	749.9	170.7	544	1510	812.9	236.8	507	1792	800	289.5	1400
TDS	235	701	355.9	114.7	244	682	374.6	108.2	215	783	364.8	120.5	1000
DO	1.1	6.8	3.6	1.446	2	10.5	4.169	1.889	1.2	9.5	4.22	1.974	5
TH	197	489	309.9	74.99	205	495	320.3	75.99	225	575	363.3	81.37	500
Cl^-	19.21	349.9	66.53	71.60	9.99	344.9	63.05	71.85	14.99	232.4	38.61	48.72	250
HCO_3^{2-}	319	514	429.8	56.49	325	525	426.3	62.03	350	750	537.5	103.1	1000
PO_4^{3-}	0.987	1.896	1.571	0.184	1.373	1.765	1.546	0.092	0.311	2.032	1.156	0.596	12
NO_3^-	0.79	2.98	1.619	0.662	0.179	9.362	1.592	1.917	0.403	5.443	1.527	1.163	50
SO_4^{2-}	17.38	45.29	26.66	7.923	17.66	40.42	24.23	6.851	17.9	42.21	25.67	7.087	400
Na	37.29	88.79	56.43	14.46	29.35	74.32	46.19	12.08	22.45	83.06	49.92	15.15	200
K	2.89	15.87	8.19	3.541	2.01	12.27	6.003	2.775	4.08	14.26	7.653	2.890	55
Mg	15.37	59.05	36.54	12.18	13.42	68.32	38.91	13.83	12.2	56.12	28.85	13.96	50
Ca	39.6	110.0	64.78	15.48	44	86	65.6	11.23	78	162	104.9	19.84	75
Cr	0.031	0.102	0.067	0.026	0.023	0.039	0.031	0.004	0.071	0.134	0.109	0.019	0.05
Fe	1.573	3.690	2.266	0.475	0.559	1.549	0.972	0.248	1.102	2.599	1.739	0.397	0.3
Mn	0.925	2.499	1.299	0.361	0.422	0.990	0.741	0.186	0.632	1.726	1.078	0.287	0.08
Ni	0.010	0.142	0.048	0.028	0.041	0.160	0.084	0.032	0.030	0.057	0.041	0.009	0.07
Cu	0.020	0.081	0.033	0.012	0.017	0.084	0.035	0.013	0.002	0.074	0.020	0.017	2
Zn	0.012	0.089	0.033	0.015	0.001	0.384	0.066	0.083	0.016	0.032	0.024	0.004	3
Cd	0.000	0.011	0.005	0.003	0.000	0.011	0.005	0.003	0.000	0.011	0.004	0.003	0.003
Pb	0.018	0.142	0.069	0.027	0	0.040	0.017	0.011	0.053	0.170	0.075	0.026	0.01

Note: EC – electrical conductivity, TDS – total dissolved solid, DO – dissolved oxygen, TH – total hardness, Cl^- – chloride, HCO_3^- – bicarbonate, PO_4^{3-} – phosphate, NO_3^- – nitrate, SO_4^{2-} – sulphate, Na – sodium, K – potassium, Ca – calcium, Mg – magnesium, Cr – chromium, Mn – manganese, Fe, – iron, Ni – nickel, Cu – cupper, Zn – Zink, Cd – cadmium, Pb – lead

The physical parameters (pH, DO, TDS, Terbitidy and EC of collected groundwater samples were determined in spot with the portable meter. The collected groundwater samples were carried to the laboratory within 8 hours. The collected samples were analyzed at Rajshahi University Central laboratory. The concentrations of metals namely Ca, Mg, Cr, Fe, Mn, Cu, Zn, Cd, and Pb were determined by atomic absorption spectrometry (AAS) (AAS220FS), graphite AAS220FS and Ion Chromatograph.

2.3. Approaches of Multivariate Statistical Techniques

Principal component analysis (PCA), hierarchical cluster analysis, and Pearson correlations, were conducted using SPSS.20 software and an ordinary kriging interpolation model was used Arc GIS (10 version). MS Excel was used to analyze basic statistical analysis, including the minimum, maximum, mean, and standard deviation.

3. Results and Discussions

3.1. Characterization of groundwater

The results from the analysis of groundwater samples as well as the geochemistry of groundwater are shown in Table 1.

Table 1 presented the investigated data of physicochemical parameters, anions, and cations of the analyzed groundwater samples (Supplementary Data Table S_1, S_2 and S_3). The ranges of pH of the investigated groundwater samples are 7.5-8.5, 7.1-7.8, and 7.9-9 (slightly alkaline) (permissible limit 6.5 to 8.5, WHO, 1997), the EC range 501-1024 µS/cm, 544-1510 µS/cm , 507-1792 µS/cm in PRM, MON andPOM, respectively, which indicates non-saline water. The major cations in the investigated groundwater samples were Ca (39.60-110 , 44.0-86, and 78.0-162 mg/L), Mg (15.37-59.04, 13.42-68.32, and 12.2-56.12 mg/L), Na (37.29-88.79, 29.35-74.32 and 22.45-88.06 mg/L), K (2.89-15.87, 2.01-12.27, and 4.08-14.26 mg/L) showed significant variation in PRM, MON, and POM, respectively. The research observed that the concentration of TDS, TH, HCO_3-, SO^{2-}, PO_4^{3-}, NO_3^-, Na^+, K^+, Cu and Zn below the WHO standard limit. Among the trace elements, the concentration range of Fe (1.573-3.690 , 0.559-1.549 and 1.102-2.599 mg/L), Mn (0.924-2.4991, 0.422-0.990, and 0.632-1.726 mg/L), and Pb (0.018-0.142, 0-0.040 and 0.049-0.170 mg/L) of the studied samples was in PRM, MON, and POM, respectively. The research noted that 100% of samples of the Fe and Mn concentrations exceeded the WHO standard limit but 100% of samples exceeded in PRM and POM whereas 65% of samples exceeded in MON.

The major anion in the investigated groundwater samples were HCO_3^-(319-514, 375-525, and 350 – 750 mg/L) whereas Cl^- (19.21-349.90, 9.99-344.89, and 14.99 – 232.482 mg/L) was the second dominant anion in PRM, MON, and POM, respectively. The SO_4^{2-}, NO_3^-, and PO_4^{3-} ion concentrations range (17.38-45.29, 17.66-40.42, and 17.90-42.21 mg/L), (0.79-2.98, 0.18-9.36, and 0.403-5.44 mg/L), and (0.99-1.90, 1.37-1.77, and 0.311-2.032 mg/L) in PRM, MON and POM, respectively below the all permissible limits. Plotting major ion composition on a Piper diagram shows that the studied groundwater samples are mostly of the Ca–Mg–HCO_3 type in the research area (Fig. 2). The investigated result showed that Ca^{2+}> Mg^{2+} > K^+ and HCO_3^-> Cl^-> SO_4^{2-} > NO_3^-> PO43-, where HCO_3^- and Ca^{2+} are dominant anion and cation, respectively. The dissolved Fe, Mn, and Pb concentration in groundwater of the research area was shown in Table 3. Table 3 also showed the Fe, Mn, and Pb concentrations of the studied 20 groundwater samples and the mean, average, and standard deviation in three seasons of the research area. The maximum Fe and Mn concentration level were 3.69 and 2.50 mg/L in PRM but the Pb concentration level was 0.17 mg/L in POM. These are many times higher than all permissible limits (BWDS, BECR, INDIA, WHO, and US-EPA).

Soil, minerals, rocks, and groundwater all naturally contain Fe and Mn. [39]. Through various dissolution mechanisms, they were released into groundwater and found in different oxidation states, such as Fe +2 and +3 and Mn +2 and +4 [40, 41]. According to their similar chemical properties, such as ionic radius, common valence charges in physiological conditions, and specific absorption mechanisms, in groundwater, Fe and Mn naturally coexist [42, 43]. According to the national hydrochemical survey [4] about 42% of tubewells have Mn concentrations above the allowable limits. In the groundwater, correlations between Fe and Mn denote the reductive dissolution of Mn and Fe-rich compounds. Geogenic processes, such as weathering and leaching of iron oxides and hydroxides containing minerals and rocks, including hematite, magnetite, pyrite, limonite, siderite, and Mn-bearing minerals, such as rhodochrosite, rhodonite, braunite, and pyrochroite, in the aquifers, are the sources of Fe and Mn in groundwater.

According to the EPA (1993) [72], iron is the second most common metal in the crust on earth. In the periodic table, iron is located in position 26. Almost all living creatures require iron for survival and growth [44]. It is one of the essential parts of living things like algae, in addition to catalase, cytochromes, and oxygen-transporting proteins like myoglobin and hemoglobin [45]. Due to its inter conversion between Fe^{2+} (ferrous) and Fe^{3+} (ferric) ions, Fe is the significant transition metal for different biological processes of redox [46].

$$2FeS_2 + 7O_2 \rightarrow 2FeSO_4 + H_2SO_4 \ (Ferrous)$$
$$4FeSO_4 + O_2 + 10H_2O \rightarrow 4Fe(OH)_2 + 4H_2SO_4 \ (Ferric)$$ Equation (1).

Pb is found in two oxidation states, +2 and +4, as a normal element in the crust of earth. At a normal pH, it exists in water as $PbOH^+$, Pb^{2+}, and $PbHCO_3^+$ ions [47]. Human exposure to even trace levels of Pb is more deadly than exposure to other heavy metals contamination [48]. Pb and Pb compounds accumulated in the soil, water, and air by human activities like, manufacturing industries, mining activities, and the combustion of fossil fuels. Pb is used to manufacture cosmetics, lead acid batteries, and metal goods including ammunition, solder, and pipes, among other things [49]. Due to its severe toxicity, Pb has been used much less frequently recently in a variety of products, including paints, gasoline, and other items. Paints containing lead, gasoline, cosmetics, toys, home dust, polluted soil, and industrial emissions are the main sources of lead exposure [50].

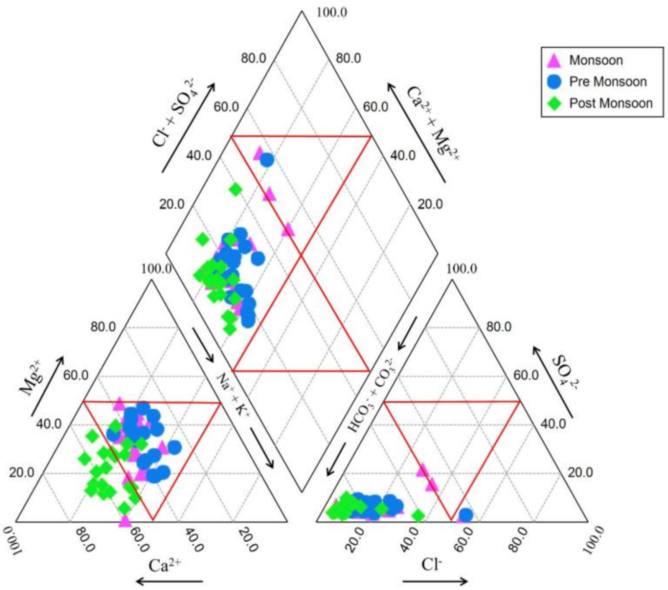

Figure .2. Piper diagram.

Groundwater contamination with metals by lead-acid battery industry activities and vehicle exhaust discharge. Pb comes from battery waste, lead pipes, industrial dust piles, vehicle exhaust discharge, fixtures, and faucets, which are the most common sources of Pb contamination in drinking water [51]. In this way, a large amount of Pb is continuously released into the groundwater by anthropogenic activity.

3.2. Water type

To explore the geochemistry and water types of the studied groundwater in the research areas, the study plotted Pipers' diagram [52]. The cations Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} and anions HCO_3^- , Cl^- , and SO_4^{2-} were used in Piper diagram to define water categories (Figure 2) in three seasons. The Piper diagram's symbolic area enables the classification of maximum water samples as clearly Ca and HCO_3^-type as wel as the water class indicated as Ca-Mg- HCO_3^-. All samples for the PRM, most of the sample for the MON, and a small number of samples for the POM lie in no dominant area and may be classified roughly as Ca-Mg- HCO_3^- type.

3.3. Water quality standards for drinking and irrigation

Standards limits of water for drinking and irrigational purpose are presented Table 2.

Table 2 illustrates variations in the permissible limits for Fe, Mn, and Pb. Various organizations fixed distinct concentrations for the same element as standard permissible limits. For instance, WHO sets a lower concentration for Mn but a higher one in the USEPA Standard. BWDS and INDIA set the Mn standard 0.1 mg/L, whereas BECR fixed the allowable limit 0.4 mg/L but the permissible limits of Fe are the same in all standards..

Table 2: Drinking and irrigational water quality standard for Fe, Mn, and Pb

Parameters	Drinking water quality standard					Irrigational water quality standard		
	BWDS[1]	BECR[2]	WHO[3]	US-EPA[4]	INDIA[5]	BIWS[6]	FAO[7]	US-EPA[8]
Fe (mg/L)	0.3-1.0	0.3-1.0	0.3	0.3	0.3	-	5.0	5.0
Mn(mg/L)	0.1	0.4	0.08	0.05	0.1	-	0.2	0.2
Pb (mg/L)	0.05	0.01	0.01	0.015	0.05	0.1	5.0	5.0

[1]Department of Public Health and Engineering, Bangladesh (2017); [2]Bangladesh Environmental Conservation Rule-2023; [3]World Health Organization, Drinking water standard, 4th ed. (2011); [4]US- EPA Drinking water standard (2018); [5]Drinking water standard for India (IS10500, 2012); [6]Bangladesh irrigation water standard (2009); [7] FAO-Water quality for agriculture (1985); [8]US-EPA-Guidelines for water reuse (2019).

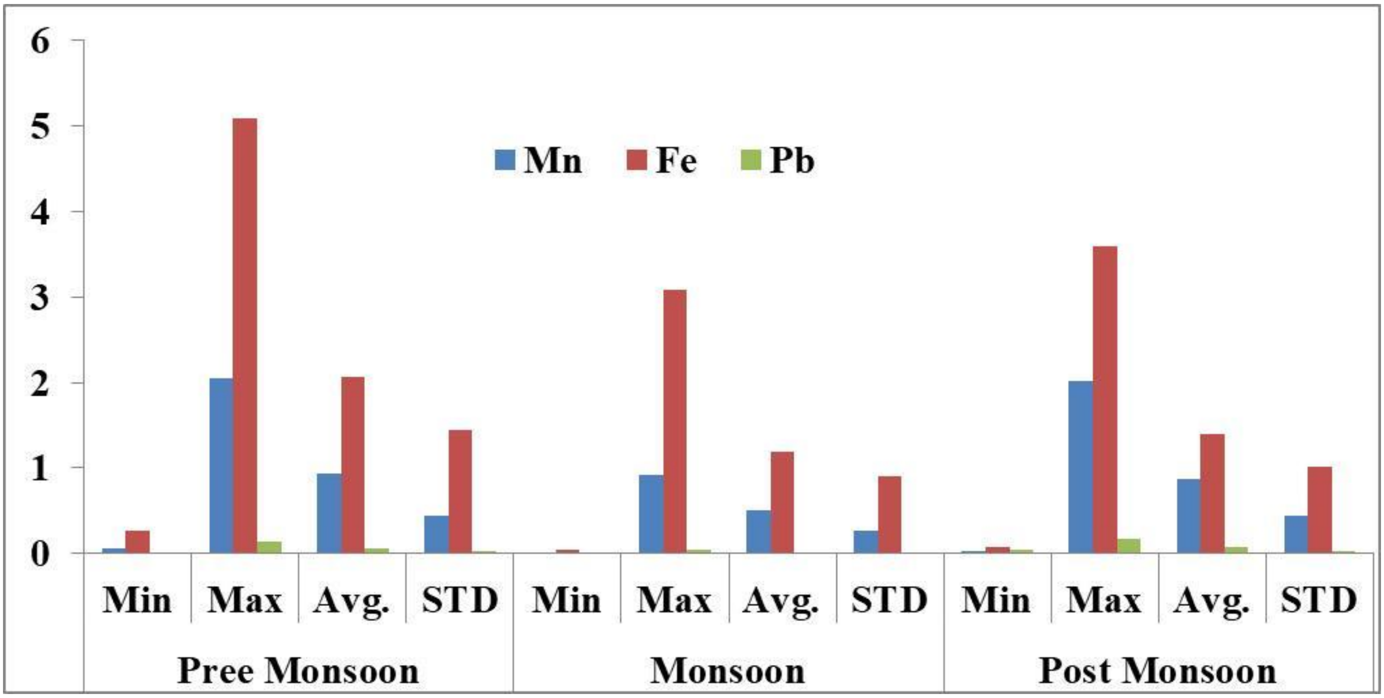

Figure 3. Summary of the concentrations of Fe, Mn, and Pb in studied groundwater samples PRM, MON and POM.

For drinking purposes regarding Pb, the BECR, WHO, US-EPA standard limits indicated 0.01 mg/L but BWDS and INDIA indicated 0.05 mg/L. However, in irrigational purposes FAO and US-EPA standard limits are the same [21]. Table 3 showed that in pre monsoon period all the Fe and Mn concentrations of investigated samples exceeded all standard permissible limits. All the Pb concentrations (100%) exceed the BECR, WHO and USEPA standard limits but 18 samples out of 20 (90%) exceed the BWDS and Indian standard limits.

The highest concentration of Fe, Mn, and Pb in the studied samples are following order: Fe (3.69) >Mn (2.50) >Pb (0.14).

During the monsoon period, 40% Fe concentrations (8 out of 20) exceeded all acceptable limits but all the samples (100%) exceeded the limits set by USEPA, WHO, and Indian standards. All the Mn concentrations exceeded all permissible limits. For Pb concentration, 13 out of 20 samples (65%) exceeded BECR, WHO, and USEPA permissible limits but all the concentration of Pb were below the BWDS and Indian standards limits. The height concentration of Fe, Mn, and Pb in the studied samples are following order: Fe (1.55) >Mn (0.99) >Pb (0.039).

In POM, all the concentrations both Fe and Mn exceeded all allowable limits. All the Pb concentrations of investigated samples exceeded the BECR and WHO standard limits but 19 concentrations exceeded the BWDS standard value. The height concentration of Fe, Mn, and Pb is the following order: Fe (2.60) >Mn (1.72) >Pb (0.17).

The research showed that all the studied samples are suitable for irrigational purposes in three seasons. Table 3 showed that observed in the data collection of three season’s pre monsoon period showed higher values for Fe (3.69) and Mn (2.50) but Pb (0.17) in post monsoon period.

3.4. Comparison the concentration of Fe, Mn, and Pb in this study with relevant published literature data

Comparison of Fe, Mn, and Pb concentration in studied groundwater samples with different areas relevant published literature data in Table 4 is the most essential to realize the regional Fe, Mn, and Pb concentration levels and regional groundwater quality.

3.5. Seasonal Variations

The research denoted the clear seasonal variation of the concentration of Fe, Mn, and Pb in three seasons. In this research the highest concentration of Fe (3.69 mg/L) and Mn (2.05 mg/L) in PRM but Pb (0.17) in POM. The results of this analysis demonstrated that, the Fe, Mn, and Pb concentrations of 100% samples exceeded the WHO standard limit in all seasons except Pb in monsoon. The study showed that in post monsoon period the Pb concentration was high. Because in monsoon Pb released into surface water through various anthropogenic activities and leached into groundwater and shows high concentration in post monsoon period. In monsoon groundwater recharge and diluted, low concentrations of Fe, Mn, and Pb were observed. The fluctuation of investigated groundwater quality parameters such as the concentration of Fe, Mn, and Pb in three seasons is illustrated in Fig-4.

The seasonal variations of Fe, Mn, and Pb concentration in the groundwater can be influenced by a variety of factors, including climatic conditions, geological characteristics, and human activities. Rainfall can significantly impact groundwater quality. Heavy rains can lead to the dilution of groundwater, potentially reduce the of Fe, Mn, and Pb concentrations. This is because rainwater can infiltrate the ground and mix with existing groundwater, lowering the overall concentrations of these elements.

Table-3. Results of Fe, Mn and Pb concentration in studied groundwater samples of Chapai Nawabganj district, Northwestern Bangladesh (PRM, MON, POM).

Sl.	Sample	Concentrations (mg/L) in PRM			Concentrations (mg/L) in MON			Concentrations (mg/L) in POM		
		Fe	Mn	Pb	Fe	Mn	Pb	Fe	Mn	Pb
1	GWS-1	2.475	1.422	0.095	0.931	0.831	0.032	1.592	1.051	0.097
2	GWS-2	2.020	1.037	0.067	0.640	0.622	0.014	1.172	0.836	0.068
3	GWS-3	2.257	1.287	0.085	0.559	0.422	0	1.659	0.945	0.097
4	GWS-4	2.023	1.016	0.051	0.929	0.819	0.028	1.102	1.016	0.053
5	GWS-5	3.024	1.655	0.091	1.125	0.920	0.028	2.215	1.423	0.063
6	GWS-6	2.065	1.065	0.051	1.385	0.990	0.033	2.346	1.518	0.073
7	GWS-7	2.059	1.135	0.051	0.775	0.512	0.009	1.924	1.015	0.053
8	GWS-8	2.679	1.485	0.018	0.970	0.606	0.009	2.125	1.206	0.063
9	GWS-9	1.882	1.623	0.071	1.263	0.926	0.014	1.660	1.121	0.073
10	GWS-10	2.491	1.292	0.057	1.549	0.811	0.023	1.815	0.981	0.058
11	GWN-1	3.690	2.498	0.142	0.676	0.983	0.005	2.599	1.726	0.169
12	GWN-2	2.022	1.125	0.084	0.986	0.612	0.009	1.513	1.025	0.087
13	GWN-3	2.265	1.427	0.032	1.065	0.927	0.023	2.002	1.049	0.088
14	GWN-4	1.938	0.924	0.064	0.738	0.547	0.014	1.652	0.925	0.057
15	GWN-5	2.022	1.210	0.054	1.093	0.910	0.040	1.832	1.054	0.063
16	GWN-6	2.067	1.585	0.053	1.099	0.810	0.023	1.599	1.140	0.053
17	GWN-7	1.573	0.994	0.065	0.914	0.602	0.023	1.114	0.649	0.068
18	GWN-8	2.031	1.051	0.085	1.050	0.913	0.009	1.890	1.511	0.072
19	GWN-9	2.726	1.072	0.057	0.788	0.519	0	1.549	0.632	0.058
20	GWN-10	2.016	1.087	0.094	0.894	0.526	0.014	1.413	0.732	0.075
	Min	1.573	0.924	0.018	0.559	0.422	0	1.102	0.632	0.053
	Max	3.690	2.499	0.142	1.549	0.990	0.040	2.599	1.726	0.1698
	Average	2.266	1.299	0.069	0.972	0.741	0.017	1.739	1.078	0.075
	STD	0.475	0.361	0.027	0.248	0.186	0.011	0.397	0.287	0.026

Table 4. Comparison the concentrations of Fe, Mn, and Pb in this study with relevant published literature data.

Sample Area		Mean value of Metals			Reference
		Fe (mg/L)	Mn(mg/L)	Pb(mg/L)	
Chapinawbganjsadar and	PRM	2.266	1.299	0.069	
Shibganjupozila	MON	0.972	0.741	0.017	This Study
	POM	1.739	1.078	0.075	
Rajshahi City		3.1	1.47	1.167	[61]
Kushtia		5.072	1.614	0.043	[10]
Southeast Suzhou City, China		0.922	0.266	0.00047	[62]
Myingyan Township, Myanmar		0.940	0.342	<1	[63]
Industrial hub of Unnao, India		0.551	0.622	0.432	[64]
Cambodia		1.392	0.2904	0.0064	[65]
Ha Nam province, Vietnam		26.475	0.675	<0.001	[66]
Vehari, Pakistan		1.62	0.82	0.1475	[67]
West Bengal, India		0.8	<0.1	<0.01	[68]
West Tripura, northeast India,		1.36	0.10	0.02	[69]
Barpeta, Assam, India		3.696	0.749	0.00285	[70]

Table 5. Pearson Correlation in PRM.

Parameter	pH	EC	TDS	DO	TH	Cl^-	HCO_3^-	PO_4^{3-}	NO_3^-	SO_4^{2-}	Na	K	Ca	Mg	Mn	Fe
pH	1															
EC	-0.13	1														
TDS	-0.05	0.37	1													
DO	-0.14	0.16	0.51	1												
TH	-0.19	0.53	0.92	0.40	1											
Cl^-	-0.08	-0.02	0.89	0.62	0.76	1										
HCO_3^-	0.16	0.68	0.73	0.39	0.78	0.47	1									
PO_4^{3-}	0.12	0.05	-0.11	0.09	-0.17	-0.15	0.04	1								
NO_3^-	0.54	0.26	0.11	-0.12	0.02	-0.14	0.36	0.50	1							
SO_4^{2-}	-0.28	0.38	0.24	0.09	0.32	0.06	0.25	0.06	-0.02	1						
Na	-0.10	0.26	0.73	0.54	0.63	0.72	0.56	-0.17	-0.16	0.38	1					
K	-0.37	0.00	-0.18	0.00	-0.11	-0.14	-0.27	0.02	-0.32	0.10	-0.03	1				
Ca	-0.10	0.25	0.89	0.44	0.78	0.84	0.55	-0.16	0.02	0.11	0.70	-0.09	1			
Mg	-0.13	0.59	0.69	0.25	0.87	0.47	0.79	-0.06	0.09	0.40	0.41	-0.15	0.37	1		
Mn	-0.22	0.23	-0.03	-0.22	-0.05	-0.20	-0.12	0.20	0.27	-0.29	-0.45	-0.12	0.03	-/012	1	-
Fe	-0.20	0.04	-0.10	-0.29	-0.07	-0.21	-0.24	0.29	0.15	-0.07	-0.48	0.14	0.00	-0.13	0.77	1
Pb	0.26	-0.07	-0.08	0.16	-0.21	-0.06	-0.07	0.27	0.28	-0.55	-0.30	-0.16	-0.10	0.20	0.78	0.44

Table 6. Pearson Correlation in MON.

Parameter	pH	EC	TDS	DO	TH	Cl^-	HCO_3^{2-}	PO_4^{3-}	NO_3^-	SO_4^{2-}	Na	K	Ca	Mg	Mn	Fe
pH	1															
EC	-0.24	1														
TDS	-0.10	0.95	1													
DO	0.20	-0.25	-0.27	1												
TH	-0.21	0.93	0.92	-0.24	1											
Cl^-	-0.04	0.87	0.85	-0.12	0.74	1										
HCO_3^{2-}	-0.44	0.82	0.73	-0.32	0.87	0.50	1									
PO_4^{3-}	0.20	-0.17	-0.03	-0.20	-0.28	-0.09	-0.38	1								
NO_3^-	-0.02	0.75	0.74	-0.24	0.61	0.90	0.38	0.06	1							
SO_4^{2-}	0.14	0.22	0.31	-0.04	0.35	0.13	0.18	-0.02	-0.09	1						
Na	0.02	0.64	0.64	0.07	0.52	0.76	0.40	-0.19	0.49	0.35	1					
K	-0.19	0.02	-0.05	-0.07	0.06	-0.08	0.12	-0.41	-0.14	0.04	-0.10	1				
Ca	0.05	0.74	0.71	-0.26	0.75	0.57	0.69	-0.18	0.49	0.08	0.46	0.14	1			
Mg	-0.31	0.84	0.86	-0.21	0.91	0.68	0.76	-0.14	0.57	0.46	0.45	-0.08	0.45	1		
Mn	0.19	-0.17	-0.11	-0.05	-0.16	-0.14	-0.18	-0.26	-0.25	0.02	-0.10	0.07	-0.15	-0.18	1	
Fe	0.40	-0.19	-0.01	0.04	-0.16	-0.11	-0.26	0.14	-0.20	0.40	0.09	-0.18	-0.18	-0.09	0.61	1
Pb	-0.21	0.03	0.09	0.08	0.02	0.08	-0.04	-0.18	-0.19	0.22	0.22	0.24	-0.10	0.08	0.57	0.57

Table 7. Pearson Correlation in POM.

Parameter	pH	EC	TDS	DO	TH	Cl^-	HCO_3^-	PO_4^{3-}	NO_3^-	SO_4^{2-}	Na	K	Ca	Mg	Mn	Fe
pH	1															
EC	-0.36	1														
TDS	-0.28	0.89	1													
DO	-0.10	0.52	0.54	1												
TH	-0.26	0.83	0.77	0.24	1											
Cl^-	-0.33	0.92	0.88	0.67	0.70	1										
HCO_3^-	-0.16	0.67	0.44	-0.01	0.60	0.38	1									
PO_4^{3-}	-0.16	0.08	0.08	0.36	0.13	0.33	-0.32	1								
NO_3^-	0.16	0.66	0.70	0.67	0.45	0.78	0.23	0.22	1							
SO_4^{2-}	-0.29	0.11	-0.01	0.00	0.13	0.04	0.00	-0.01	-0.11	1						
Na	-0.24	0.70	0.54	0.34	0.44	0.64	0.49	-0.12	0.41	0.50	1					
K	-0.31	-0.21	-0.22	-0.07	-0.43	-0.21	-0.01	-0.13	-0.20	0.18	-0.08	1				
Ca	-0.02	0.79	0.77	0.37	0.69	0.68	0.70	-0.13	0.76	0.03	0.57	-0.17	1			
Mg	-0.15	0.22	0.29	0.04	0.49	0.27	-0.04	0.41	-0.06	0.21	0.15	-0.48	-0.01	1		
Mn	0.12	0.00	-0.07	-0.40	0.30	-0.19	0.35	-0.09	-0.35	-0.01	-0.13	-0.17	0.07	0.24	1	
Fe	0.10	0.05	0.06	-0.36	0.32	-0.10	0.17	-0.10	-0.22	0.19	0.01	-0.26	0.10	0.45	0.81	1
Pb	0.16	-0.14	-0.18	-0.01	0.11	-0.23	0.02	0.13	-0.20	-0.29	-0.35	-0.25	-0.14	0.31	0.47	0.45

Table 8. Principal component analysis (PCA) of metals in three seasons.

Rotated Component Matrix														
Parameter	PRM					MON					POM			
	PC1	PC2	PC3	PC4	PC5	PC1	PC2	PC3	PC4	PC5	PC1	PC2	PC3	PC4
Na	-.431	**.804**	.190	-.027	-.076	**.836**	-.014	.252	-.204	.148	.130	.066	**.844**	.014
K	-.062	-.081	-.200	**.835**	.202	.016	.053	.037	.037	-.954	.163	-.306	**.706**	.063
Ca	.069	**.906**	.276	.070	.076	.401	-.238	**.610**	-.320	-.099	.262	-.066	-.633	**.377**
Mg	-.073	.176	**.917**	-.088	.017	.304	-.050	**.800**	.090	.107	-.408	.483	-.370	-.466
Cr	-.153	-.746	**.615**	.015	.021	-.002	.045	.336	**.559**	**.553**	**.861**	-.075	.209	.002
Mn	**.917**	-.047	-.060	-.040	-.149	.037	**.838**	-.199	-.080	-.092	.145	**.885**	.030	.038
Fe	**.841**	-.125	.000	.212	-.177	-.069	**.816**	-.025	-.366	.233	.176	**.927**	-.136	.019
Ni	-.205	.298	**.428**	.310	-.083	**.942**	.082	-.163	-.100	-.003	**.643**	.099	.242	.391
Cu	-.136	-.101	-.170	-.728	**.170**	-.640	-.240	-.101	-.255	**.265**	.026	.128	-.139	**.908**
Zn	**.890**	-.004	-.035	.106	.093	.319	-.029	-.836	-.072	.013	**.807**	.007	.007	.387
Cd	-.090	.005	-.003	.006	**.978**	-.109	-.258	-.051	**.884**	-.040	**.769**	.245	-.184	-.156
Pb	**.684**	-.001	-.191	-.216	.042	.210	**.842**	.093	.070	-.127	-.542	**.648**	.023	.210
% variance	28.54	17.47	12.59	11.44	8.60	23.45	20.52	14.05	10.91	10.61	28.44	22.07	13.88	10.58
% Cumulative	28.54	46.00	58.59	70.14	78.77	23.45	43.96	58.02	68.93	79.53	28.44	50.51	64.39	74.97
Eigen Value	3.42	2.09	1.51	1.39	1.04	2.81	2.46	1.69	1.31	1.27	3..41	2.65	1.67	1.27

The Fe and Mn concentrations in groundwater can vary with the effects of redox conditions. During the wet season, increased moisture and changing water levels can influence the oxygen content of groundwater, affecting the solubility of Fe and Mn. In oxygenated conditions, these elements may become more oxidized and less soluble, leading to lower concentrations. Farming practices and irrigation can introduce different chemicals into the soil and groundwater. For example, the use of fertilizers and pesticides could affect the composition of groundwater. These activities might vary seasonally; affecting the presence of Fe, Mn, and Pb. Seasonal changes in groundwater levels can influence the movement of groundwater through different geological formations. As water flows through various rock layers, it can interact with different minerals, potentially dissolving or leaching trace elements like Fe, Mn, and Pb.

Anthropogenic contamination sources, such as mining, industrial discharges, and waste disposal, can introduce Pb into groundwater. Pb concentrations may fluctuate due to seasonal variations in these activities. The geological composition of the area plays a significant role in groundwater quality. Groundwater from specific geological formations may have elevated levels of Fe, Mn, and Pb. The study observed that seasonal variations in the investigated data of three seasons. The figer-5 showed the higher values for Fe and Mn are obtained in PRM but higher values for Pb in POM. The intensity of these metals contamination of the groundwater in the research area follows the trend: Fe> Mn> Pb in three seasons. Microplastics transport heavy metals like Fe, Mn, and Pb to edible crops [77, 78, 79].

3.6. Pearson Correlations

A Pearson correlation matrix was utilized to explore potential correlations among these trace metals and investigate the presence of certain elements in a sample enhances the likelihood of other metals occurring or if their coexistence is a result of anthropogenic or geogenic activities in the research areas.

Tables 5, 6, and 7 summarize the inter-parameters coefficient of correlation in groundwater of three seasons. To realize the flow paths and valuable information on metal sources [71] the relationships of metal and inter-metal with other relevant parameter is very significant. Strong and statistically significant positive correlations (r>0.7) were found in several heavy metal pairs by correlation analysis.

The research showed the correlation of Fe and Mn with several influencing variables showed in three seasons strongly positive correlated with each other (Table 5, 6, 7) which indicate that the dissolution mechanism of rock source into groundwater is same.

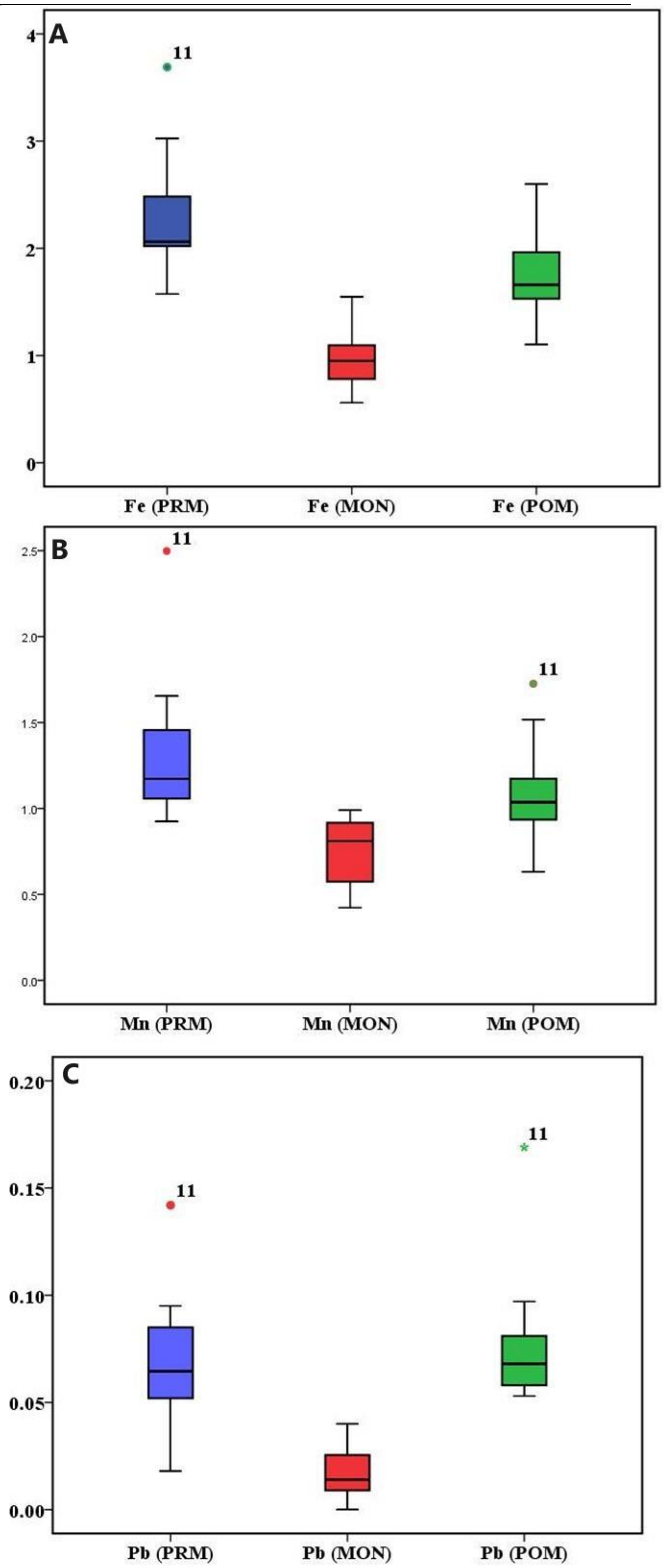

Figure 4: Box plot for Fe, Mn, and Pb concentrations in three seasons.

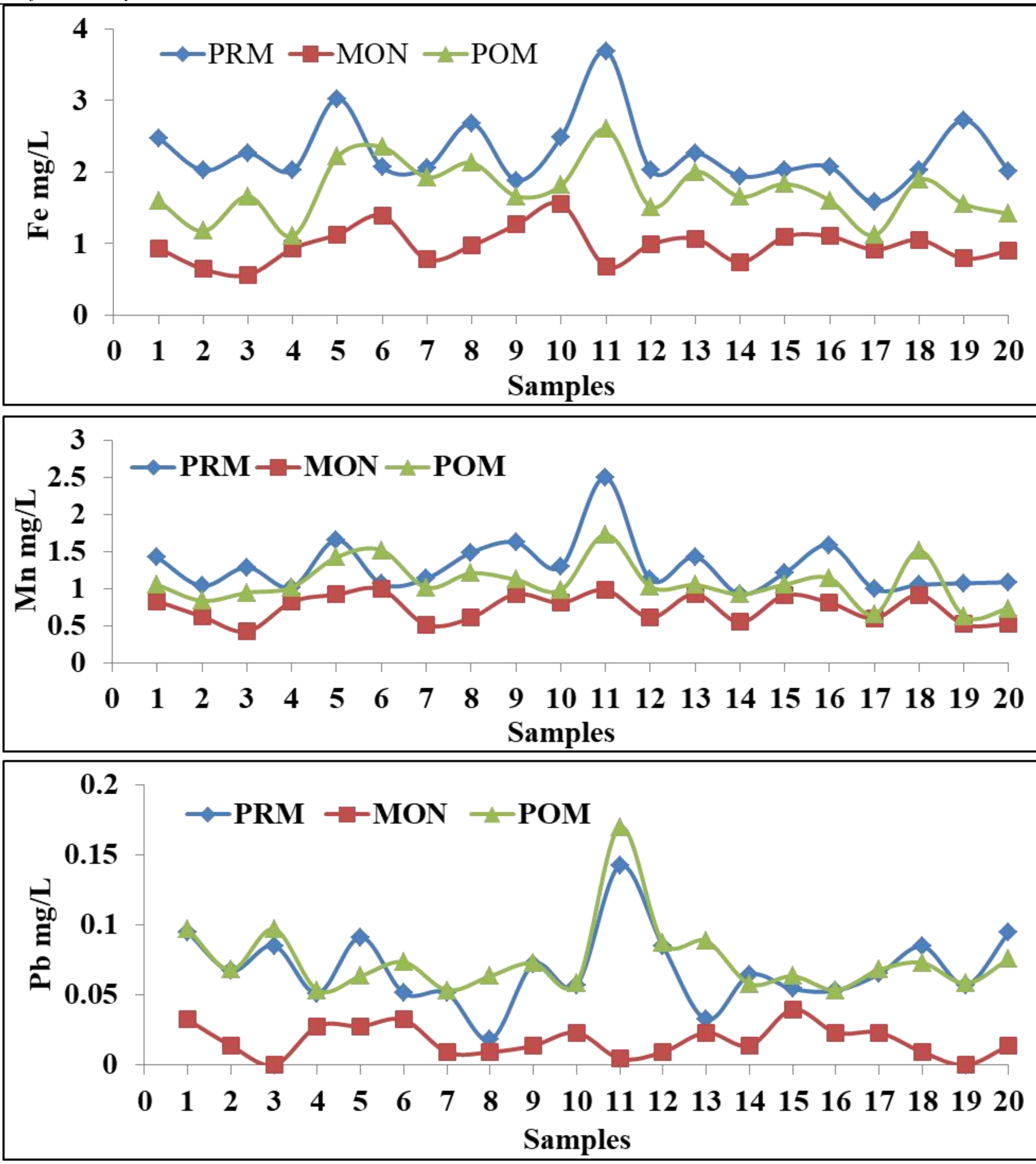

Figure 5: Scattered plot for seasonal variation of Fe, Mn, Pb concentration in three seasons

Pb and Mn. Pb and Fe were positive correlated (< 0.5) in PRM and POM but Pb and Mn, Pb and Fe were positive correlated (> 0.5) in MON. It is seen that correlation amongst Fe and Mn, Fe and Pb, Mn and Pb with one another in three seasons are positively correlated and hence is significant at the > 0.4 level.

3.7. Fe, Mn and Pb distribution in groundwater of the research area

Heavy metals including Fe, Mn, and Pb contaminated water lead to a substantial risk for food production because agricultural soil is contaminated by several heavy metals [80, 81]. Statistical analyses of the data reveal the non-uniform distribution of these metals in the research area.

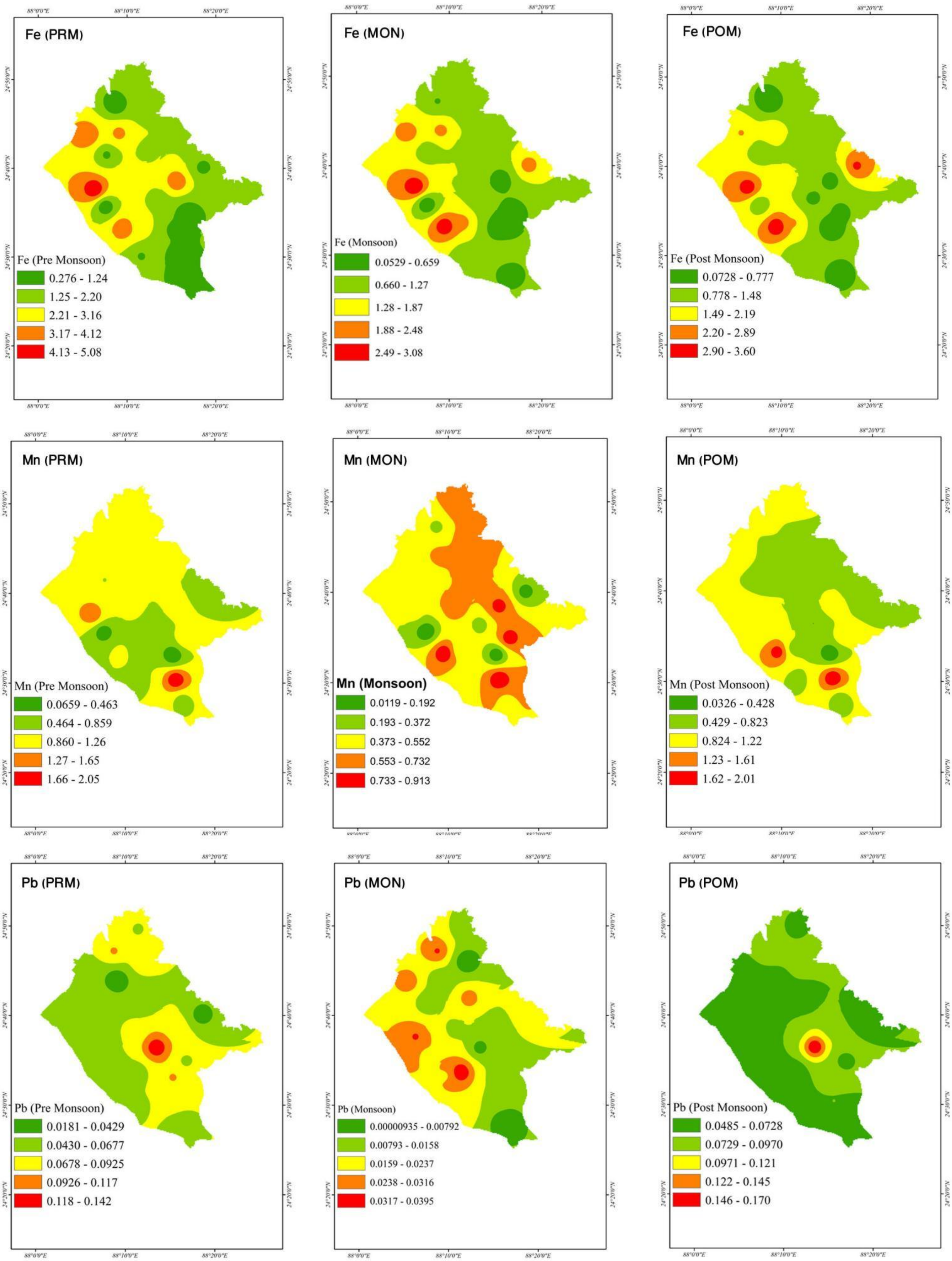

Figure 6. Spatial distributions of Fe, Mn, and Pb concentrations in the groundwater of the research area in three seasons

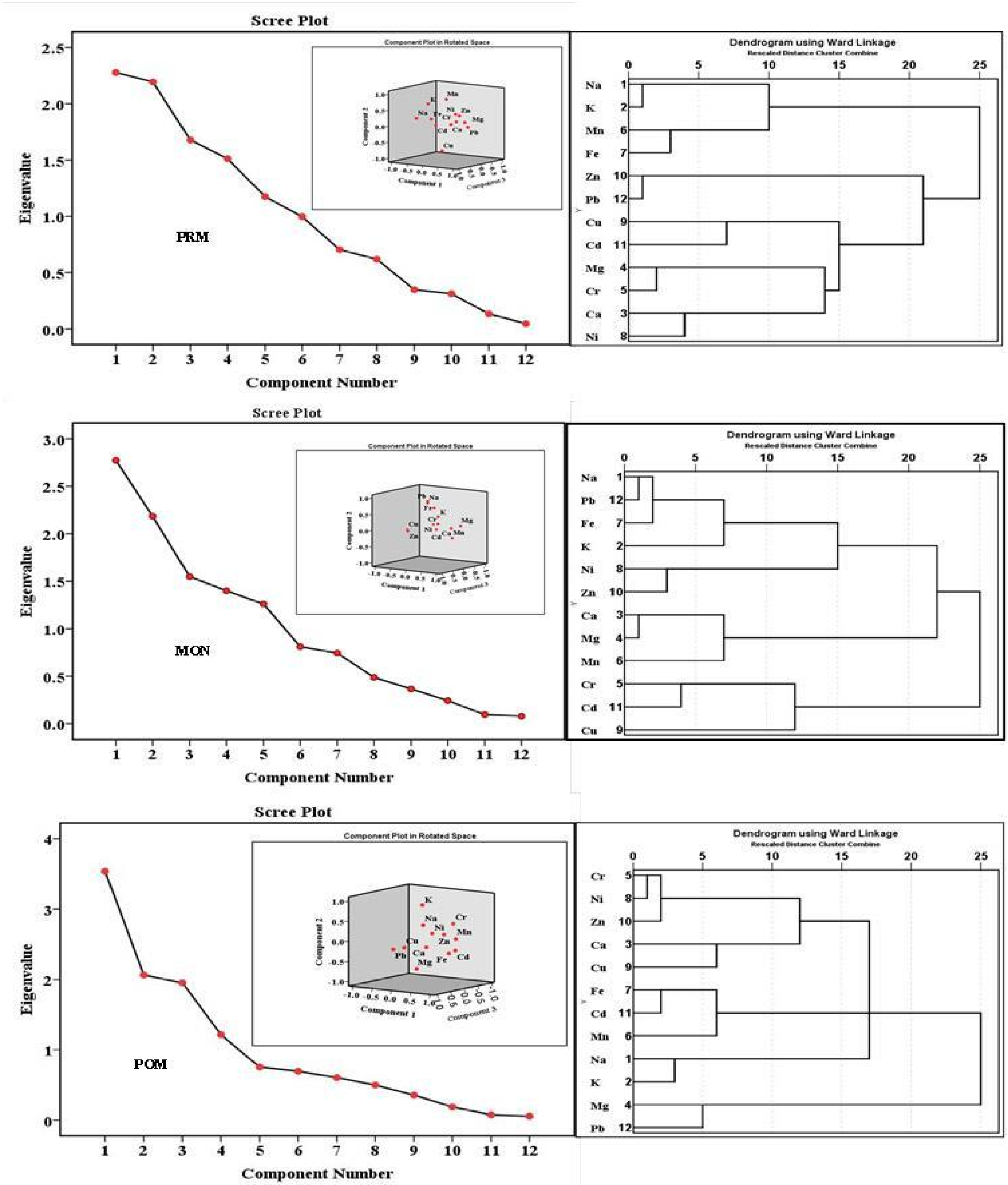

Figure7. Scree plots with component plot in rotated space and hierarchical cluster (Water parameter-based clusters) in three seasons.

To determine the distribution normality for Fe, Mn, and Pb statistical analysis was computed for three seasons. The maximum concentration of Fe was found 3.69 mg/L in the northern part of the research area (GWS-3) under Shibganj Upozilla (Fig.6) in PRM and the lowest Fe concentration was found 0.56 mg/L in MON at the middle of the study area (GWN-1). Mn (mg/L) concentrations were shown in the Fig.6 revealed that the maximum Mn concentration (2.50mg/L) was at the northern part of the study area (GWS-3)under Shibganj Upozilla (Fig.7) in PRM, whereas the lowest concentration was found 0.42 mg/L in the MON at the middle of the study area (GWN-1). Pb (mg/L) concentrations were shown in the Fig.6 revealed that the maximum Pb concentration (0.17mg/L) was at the middle point (GWN-1) of the research area under

Chapai Nawabganj Sadar, whereas the minimum concentration of 0.0092 mg/L was found in Shibganj (GWS-7, 8) of the research area.

3.8. Principal Component Analysis (PCA)

Table 8 illustrates PCA of detected water parameter in three seasons and figure 7 scree plot with component plot in rotated space and hierarchical cluster (water parameter-based clusters) in three seasons.

To analyze the geographical and compositional trends between the examined groundwater samples and the identified latent components, identify the trace metals' potential sources in the groundwater. PCA is frequently applied to categorize the contribution of both geogenic and anthropogenic pollution sources.

Factor analysis is produced four PCs in POM and five PCs in PRM and MON of R-mode factors with Eigenvalues > 1 (Table 6). The percentage of variation for these factors in three seasons is as follows: Eigenvalue >1 for PRM (28.54, 17.47, 12.59, 11.44, and 8.60%), MON (23.45, 20.52, 14.05, 10.91, and 10.61%), and PM (28.44, 22.07, 13.88, and 10.58%). The presence of high positive factor values in PRM PC1 (Mn (.917), Fe (.841), and Pb (.641); MON PC2 (Mn (.838), Fe (.816), and Pb (.842); and POM PC2 (Mn (.885), Fe (.927), and Pb (.648) all indicate that those metals are strongly associated and have dissociated from a similar type of source, which may be an exogenous discharge [76]. The cluster groups in three seasons have been done based on a dendrogram by using Ward's method (Fig. 8). Although the correlation analysis largely attributes the geogenic processes as the source of Fe and Mn, this class is composed of features irregular to anthropogenic sources as opposed to mineral dissolution. Heavy metals are poisonous substances [82]. Reports of trace metal-rich mineral or soil deposits have been made, and these potentially hazardous elements could be released into groundwater systems based on the geological context of the research location [16, 73, 74, 83, 84].

4. Conclusions

The findings of this research exposed significant seasonal variations of Fe, Mn, and Pb in three seasons. The findings showed that 100% of the samples had Fe concentrations above all allowable levels during the PRM and POM, however only 40% of the samples under study had Fe concentrations above all allowable limits during the MON. On the other hand in three seasons, all the concentrations of Mn exceeded all allowable limits. Pb concentration exceeded 100% BECR, 90% BWDS and WHO permissible limits in pre monsoon. In the monsoon period 65% of samples exceeded BECR and WHO permissible limits but all concentration were below the BWDS and Indian standard limits. In post monsoon Pb concentration exceeded 100% of BECR and WHO, 95% of BWDS permissible limits. But all the samples are suitable are irrigation purposes. The trend metal contamination in the study area follows Fe>Mn>Pb in three seasons. The concentration of Fe, Mn, and Pbare following order: pre monsoon-Fe (3.690)>Mn (2.499) >Pb (0.142), monsoon- Fe (1.549)>Mn (0.990) >Pb (0.040), and post monsoon- Fe (2.599) >Mn (1.726) >Pb (0.169). The study noted that pre monsoon period showed higher values for Fe and Mn concentration but Pb in POM period

The research indicated that the water categories of the studied groundwater samples were mainly influenced by the Ca-Mg-HCO_3 hydrochemical facies where Ca is the dominant cation and $HCO_3^-$is the dominant anion with elevated level of Fe, Mn and Pb but low levels of SO_4^{2-} , NO_3^- , and PO_4^{3-}. The study indicated that geogenic processes are the sources of Fe and Mn in groundwater, such as weathering and leaching of Fe and Mn contain rocks and minerals like pyrite, limonite, hematite, magnetite, siderite, rhodochrosite, rhodonite, braunite, pyrochroite, and manganite. But Pb is discharged into the groundwater continuously by human activities, like battery waste, lead pipes, industrial dust piles, and vehicle exhaust discharge. The extent of these metal contaminations of the local groundwater is established by this investigation. Therefore, it is necessary to choose the right treatment for future water use in the region and too appropriately preserve the water sources from any potential contamination with these trace metals Fe, Mn and Pb. Appropriate programs should be developed by the government and non-governmental organizations for reducing the level of heavy metal contaminations in drinking water.

Conflicts of Interest

There are no conflicts of interest reported by the authors.

Authors contribution

Md Zahidul Islam: Conceptualization; methodology; investigation; sample collection; sample analysis, data curation; data analysis, writing-original draft.

Md. Golam Mostafa: Conceptualization; methodology; investigation; project administration; validation; software; supervision; writing-review & editing.

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Data Availability statement

All the data support this article will be provided on request from the corresponding author.

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