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Assessment of arsenic contamination in groundwater of the Rajpur Municipality, Rautahat District, Nepal

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ABSTRACT

This study examines arsenic contamination in groundwater wells in the Rajpur Municipality, Rautahat District, Nepal. Susceptibility of arsenic effects in the Terai region is the main reason to select Rautahat District for the study. Forty-five samples of groundwater wells were collected from nine wards (Pipra Bhagwanpur, Phatuha Maheshpur, Damarchuk, Rajpur Farhadwa, Kudiya, Akolwa, Baluwa, and Bairiya) in shallow wells (<50 m, 80%) and deep wells (>50 m, 20%). The depths of the wells ranged from 7.6 to 82.4 m. The arsenic in 28.9% of the groundwater wells were within World Health Organization (WHO), 2017, drinking water quality guideline value of 0.010 mg/L. The samples of 80.0% of groundwater wells were within Nepal drinking water quality standard (NDWQS), 2022, for arsenic of 0.050 mg/L. The arsenic, iron, and manganese concentrations were in the range of below the detection limit (BDL) to 0.220 mg/L, BDL to 6.30 mg/L, and 0.04 to 1.50 mg/L, respectively. Additionally, the mean concentrations of arsenic, iron, and manganese were recorded as 0.040 mg/L, 0.78 mg/L, and 0.39 mg/L, respectively. The low Oxidation Reduction potential (ORP) in most of the groundwater wells indicates that the mobilization of arsenic, iron, and manganese in the groundwater is favorable in reducing environment. A slight positive correlation between pH and arsenic implies that arsenic mobilization is favorable at high pH. Similarly, the slight negative correlation between arsenic and depth of the groundwater wells visualizes elevated levels of arsenic in the shallow groundwater wells. There are positive correlations between arsenic, iron, and manganese. In addition, principal component analysis (PCA) indicates common natural sources for these metals. Spatial distribution patterns reveal elevated levels of EC, iron, manganese, and arsenic in many wells, indicating high mineralization.

Keywords: Groundwater Contamination; Arsenic; Iron; Manganese; Mineralization

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INTRODUCTION

Various heavy metals, such as manganese, lead, cadmium, mercury, and arsenic, are intrinsic groundwater contaminants and pose potential biohazardous risks (Järup, 2003; Mitchell et al., 2011). Arsenic, a highly toxic metalloid, exhibits brittleness, crystallinity, and lacks odor and taste in its elemental state. It has an atomic number of 33 and occurs naturally within the earth's crust (Hammond, 2000). The most common ores of arsenic are arsenian pyrite ($Fe(S,As)_2$), arsenopyrite (FeAsS), loellingite ($FeAs_2$), realgar (AsS), orpiment (As_2S_3), cobaltite (CoAsS), niccolite (NiAs), and scorodite ($FeAsO_4.2H_2O$) (Dedititus et al., 2008; Lu and Zhu, 2011; Smedley and Kinniburgh, 2013). Arsenic exists in four oxidation states, +V (arsenate), +III (Arsenite), 0 (arsenic), and −III (arsine) (Raju, 2022). In the natural waters, inorganic forms of arsenic, such as arsenite As (III) or arsenate As (V) are more common depending on redox conditions (Ferguson and Gavis, 1972; Smedley and Kinniburgh, 2013). The As (V) consists of arsenic acid (H_3AsO_4) and its conjugate bases ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}).

The ultimate sources of arsenic include natural (geology, volcanic eruption), human activities like mining, burning of fossil fuels, and pesticide application (Garelick et al., 2009). The mobilization of arsenic generally occurs between pH 6.5 to 8.5 in both oxidizing and reducing environments (IPCS, 2001; Smedley and Kinniburgh, 2013; Wang and Mulligan, 2013). In the pH range of most natural waters, the predominant As (V) species are the anions $H_2AsO_4^-$ and $HAsO_4^{2-}$. In aerobic environments, As (V) is dominant, usually in the form of arsenate (AsO_4^{3-}) in various protonation states: H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} (IPCS, 2001; Lu and Zhu, 2011). Arsenic is either adsorbed into the surface or coprecipitated in Fe/Mn oxyhydroxides (Pierce and Moore, 1982; Kim et al., 2002) and its dissolution and desorption in a reducing environment were observed by many researchers (Biswas et al., 2011; Anawar et al., 2003; Mcarthur et al., 2004; Smedley and Kinniburgh, 2013; Ni et al., 2016).

Under acidic and moderately reducing conditions, As (V) may coprecipitate with or adsorb to iron oxyhydroxides. The coprecipitates are stable under these conditions but the release of arsenic is favored with the increase in pH (Dzombak and Morel, 1991). Under reducing conditions, As (III) is prevalent in the form of arsenite (AsO_3^{3-}) and its protonated forms: H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ (IPCS, 2001; Smedley and Kinniburgh, 2013). In addition, under the aerobic and acidic to near-neutral conditions typical of many natural environments, arsenic is strongly adsorbed by Fe/Mn oxyhydroxides as arsenate ion, which results in a low concentration of arsenic. Likewise, in the aerobic and acidic to near-neutral conditions typical of many natural environments, arsenic is highly adsorbed by oxide minerals as an arsenate ion (Dzombak and Morel, 1991).

It is noted that the concentration of iron and manganese is pH dependent and higher aggressiveness of iron in low pH (Helena et al., 1999). Arsenic mobilization is highly triggered by oxides of iron (Bauer and Blodau, 2006) and manganese

(Rodrigues et al., 2016). The oxidation of the reductant would lead to the reduction and solubilization of iron and manganese (Palmucci et al., 2016; Khozyem et al., 2019). Arsenic has several inorganic and organic compounds in which inorganic arsenic is more toxic than organic (Donohue and Abernathy, 1999). However, arsenic concentration is decreased with the high conductivity of sandy soil in shallow water but except in sandy soil it is increased with the high conductivity water (Aziz et al., 2008).

Arsenic dissolved in water is toxic and can lead to several health problems. Long-term exposure to arsenic in drinking water possesses carcinogenic effects on the skin, lungs, bladder, and kidney (Anawar et al., 2002). Moreover, exposure routes i.e., food chain and air movement over time to arsenic in drinking water lead to health problems like arsenicosis, hyperkeratosis, changes in pigmentation, disturbance of the cardiovascular and nervous system functions, and finally death (Wang et al., 2019). In addition to this, malnutrition may aggregate the effects of arsenic in blood vessels (Chen et al., 1998).

Nepal is a mountainous country sandwiched between India and China. The Terai region of the country resides in the Nepal Gangetic Plain and forms the northern extension of the Indo-Gangetic Plain which represents 20 districts in the southern part bordering India and approximately 33 km away from Bangladesh comprising a width and length of 40 km and 885 km, respectively. The geology of the Terai region is similar to the Bengal Delta Plain (Thakur et al., 2010). In the alluvial aquifers of the Bengal Basin, the elevated concentration of arsenic is probably due to inputs of immature sediment from Himalayan erosion (McArthur et al., 2004).

Arsenic has been detected in alluvial aquifers of the Terai region of Nepal. Sharma (1999) studied arsenic in the groundwater wells of the Jhapa, Morang, and Sunsari districts of eastern Terai of Nepal. The study showed the existence of elevated levels of arsenic. Gurung et al. (2005) carried out a study to assess arsenic contamination in shallow groundwater wells (<50 m depth) in Nawalparasi, western Terai region of Nepal. Kanel et al. (2005) studied arsenic in groundwater wells of the Gaur Municipality, Rautahat District, Nepal. In addition, Kayastha and Pradhanang (2021) also studied the contamination of arsenic in the Bara District, Nepal. These studies revealed that the reducing groundwater environment is favorable for the mobilization of arsenic.

Rajpur Municipality lies in alluvial plain aquifers of the Terai region of Nepal where the problems of arsenic in drinking water are severe and people are affected from diseases like arsenicosis. The groundwater resources are used for drinking, irrigation, and other purposes. This study focuses on the assessment of arsenic contamination in groundwater wells and on characterizing groundwater quality based on pH, ORP, conductivity, iron, manganese, and arsenic. In addition, the study also aims to illustrate the spatial distribution pattern of arsenic, iron, and manganese, and identify influential physicochemical parameters of the groundwater wells. The findings of this study visualize the quality of groundwater resources in terms of arsenic, iron, and manganese. Furthermore, it provides insight into the drinkability of the water and realize the need for water treatment technology to remove arsenic from the groundwater.

MATERIALS AND METHODS

Study area

Rajpur Municipality is situated within Madhesh Province of Nepal with elevation ranging from 300 to 1000 m, consists of nine wards with a total area of 1126 km^2, households of 8992, and a population density of 60905 per km^2. The average minimum and maximum temperatures recorded are 19.6^{o}C and 31.1^{o}C, respectively and annual precipitation is about 1200-1300 mm (Rajpur Municipality, 2020).

The groundwater wells (shallow and deep) are the major sources of drinking water and are surrounded by agricultural land in the Rajpur Municipality. In the area, urea and potash are the common fertilizer followed by zinc, complex, and super phosphate (Sapkota et al., 2021). Super phosphate could be one of the arsenic sources (Jayasumana et al., 2015). This area is a flat and fertile region formed by sediment deposited by rivers over time and clayey loams to sandy loamy types of soils are common in the area (Poudel et al., 2002). The geology of the municipality is classified as a recent formation (DoMG, 1994) consisting alluvial deposit with coarse gravels in the north near the foot of the mountains, gradually becoming finer southward (Sharma, 1995; Upreti, 1999; Shrestha et al., 2018). This area is dominated by unconsolidated sedimentary deposits including sandstone, siltstone, and claystone (Sharma 1995; Poudel et al., 2002). In these regions, shallow aquifers (<50 m) are generally unconfined or semi-confined, whereas deep aquifers (>50 m) are predominantly confined by clay layers (Gurung et al., 2005).

Analysis of physicochemical parameters

Groundwater samples were collected from nine wards of the Rajpur Municipality in the winter season (February 2020). Forty-five water samples, five from each ward were collected (Fig. 1). The depths of groundwater wells, shallow well (<50 m) and deep wells (>50 m), were in the range of 7.6 to 82.4 m. The sampling points in each ward were selected based on a random sampling technique. The collected samples were filtered through 0.45-micron membrane filter with the help of a syringe. The syringe filters were used to collect water samples by removing other sediments and unwanted particles from the samples. The samples for iron and manganese were preserved by adding 0.5 mL/L of concentrated nitric acid. The samples for arsenic were preserved with hydrochloric acid (adding 4-5 drops in 500 mL of the sample). These samples were then brought to the laboratory for analysis. The samples were kept at 4°C before analysis. The measurements of temperature, oxidation reduction potential (ORP), electrical conductivity (EC), and pH were carried out at each sampling location. The ORP and pH were measured by Hanna HI 8314 pH/ORP meter (Italy). The EC was measured by Jenway 4200 conductivity meter (UK). The probes were calibrated before each sampling trip. The analysis of arsenic and manganese was carried out in the laboratory of Nepal Environmental and Scientific Services Pvt. Ltd., Thapathali, Kathmandu, Nepal, while the iron was measured in the laboratory of the Central Department of Environmental Science, Tribhuvan University, Kathmandu, Nepal.

Arsenic and iron were measured by spectrophotometric silver diethyldithiocarbamate and phenanthroline methods, respectively using a UV spectrophotometer (SSI 2101, China) as per APHA-AWWA-WEF (2017). Manganese was determined by atomic absorption spectrometric direct-air–acetylene method using atomic absorption spectrometer (GBC SavantAA, Australia) as per APHA-AWWA-WEF (2017). The instrumental detection limits for arsenic, manganese, and iron were 0.010 mg/L, 0.01 mg/L, and 0.10 mg/L, respectively.

Statistical and spatial analysis

Spearman's rank correlation coefficient and principal component analysis (PCA) were applied to evaluate the associations, relationships, and influences of the monitored physicochemical parameters. IBM-SPSS (19.0) was used for statistical analysis. Arc GIS (10.3) was used for mapping and spatial analysis. For the data analysis, firstly data were checked for their normality by using the Shapiro-Wilk test. Spearman rank correlation coefficient was used to observe the correlations between arsenic, manganese, iron, depth, and ORP as the data were not normally distributed.

RESULTS AND DISCUSSION

Groundwater quality

The summary of statistical data for the monitored physicochemical parameter is presented in Table 1. The pH exhibited a range of 8.01 to 8.96 (mean=8.40), while the EC ranged from 402 to 2555 µS/cm (mean=899.7 µS/cm), and the ORP displayed variation from -163 to 121 mV (mean=-85.2 mV). The concentrations of iron, manganese and arsenic varied greatly from BDL to 6.25 mg/L (mean=0.79 mg/L), 0.04 to 1.50 mg/L (mean=0.40 mg/L) and BDL to 0.220 mg/L (mean=0.040 mg/L), respectively.

The EC in the groundwater wells of the Rajpur Municipality was high due to the presence of dissolved ionic substances in the groundwater. Kanel et al. (2005) also observed EC ranging from 283 to 2457 µS/cm in the Gaur Municipality, Rautahat District, Nepal. The study by Gurung et al. (2005) indicated that ORP in the groundwater wells in Nawalparasi District, Nepal ranged from -99 to 143 mV (mean = -38.8 mV). The mean ORP of groundwater wells in the Rajpur Municipality was observed to surpass that of Nawalparasi District, Nepal suggesting a state of pronounced reduction within the groundwater environment. The negative ORP represents that the groundwater is in a reducing condition and causes high mobilization of minerals and metals. On the contrary, a study carried out by Kanel et al. (2005) recorded ORP ranged between 81 to 142 mV in Gaur Municipality, Rautahat District. Despite the elevated ORP, low nitrate, and relatively high iron and manganese concentrations depict that groundwater wells were in reducing environment.

Kanel et al. (2005) evidenced arsenic concentration of 0.001 to 0.062 mg/L in the Gaur Municipality. According to Thakur et al. (2010), there was higher arsenic concentration in the groundwater wells of Rautahat District and observed >0.050

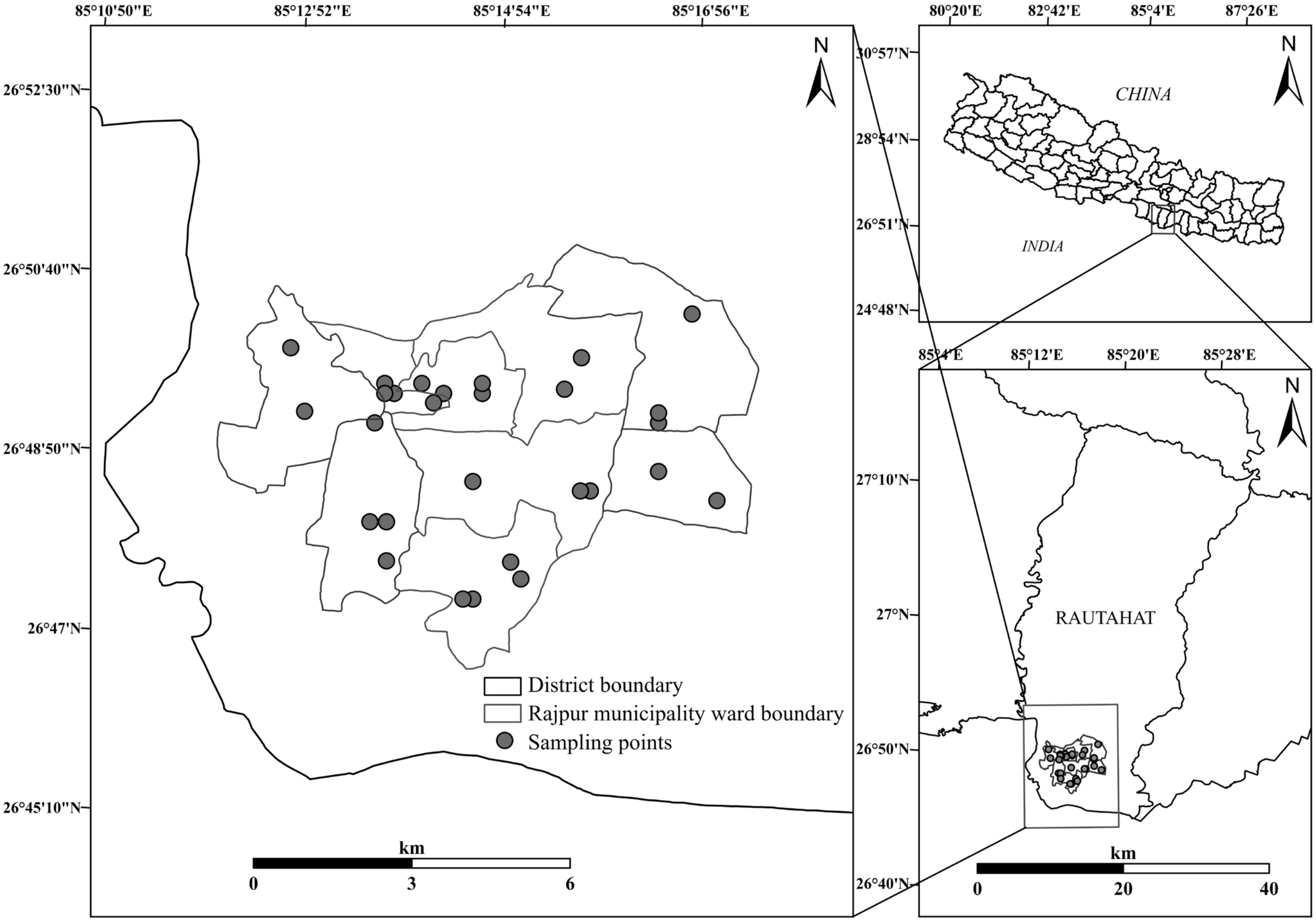

Fig. 1: Sampling points in the study area (Rajpur Municipality, Rautahat District, Nepal).

Table 1: Summary of statistical data for physicochemical parameters

Variables	Unit	Min	Max	Mean	Med	SD
pH		8.01	8.96	8.40	8.49	0.23
EC	µS/cm	402	2555	899.7	789	381.70
ORP	mV	-163	121	-85.19	-102	59.12
Fe	mg/L	BDL	6.26	0.79	0.10	1.50
Mn	mg/L	0.04	1.50	0.40	0.27	0.40
As	mg/L	BDL	0.220	0.040	0.030	0.050

BDL: Below detection limit, SD: Standard deviation

mg/L with an average of 0.007 mg/L. Chitwan District, Nepal also observed a high arsenic concentration in groundwater wells with an average of 0.53 mg/L (Lamichhane and Singh, 2019). So, the higher concentration of arsenic in the groundwater of the Rajpur Municipality may be due to higher values of iron, manganese, and the reduced environment as indicated by the high negative ORP. Many investigators also have pointed out the release of arsenic into the groundwater due to the natural source under the reductive processes (Kim et al., 2002; Smedley and Kinniburgh, 2013; Shrestha et al., 2016).

Contaminated groundwater sources with elevated concentration of arsenic in the study area may be due to the geological setup, their origin, and arsenic-bearing rocks and minerals. The leaching of arsenic from natural rocks might be the main source of groundwater contamination in the study area (Yadav et al., 2015).

Most of the groundwater wells in the study exhibited elevated levels of arsenic, iron, and manganese. The samples of 20% of groundwater wells exceeded the arsenic concentration of 0.05 mg/L and are regarded as vulnerable groundwater wells in Nepal (Table 2). So, to ensure the public health and community safety, it is vital to regularly analyze water, implement arsenic removal systems, and install deep groundwater wells, which have low risk of arsenic contamination compared to shallow groundwater wells. It is suggested to avoid arsenic rich water for irrigation to prevent soil and crop contamination. Flooding in the area can infiltrate and mobilize arsenic into the groundwater. Conducting geochemical and geological studies is essential to understand and manage arsenic contamination effectively.

Table 2: Arsenic in groundwater wells

Arsenic concentration (mg/L)	Number of groundwater wells	Percentage (%)
BDL - 0.010	13	31.2
0.011 - 0.050	22	48.9
>0.05 (Vulnerable)	9	20.0
Total	45	100

The concentration of arsenic was compared with World Health organization (WHO), 2017 guideline for drinking water (WHO, 2017) and Nepalese National drinking water quality standard (NDWQS), 2022 (GoN/MoWS, 2022). Besides, the concentrations of iron and manganese were compared with NDWQS (2022). The samples of 71.2 % of groundwater wells exceeded WHO (2017) guideline value for drinking water of 0.010 mg/L for arsenic. The samples of 28.9 % of groundwater wells exceeded NDWQS (2022) value of 0.30 mg/L for iron and 56.6% exceeded the NDWQS (2022) value of 0.20 mg/L for manganese (Table 3).

Table 3: Comparison of arsenic, manganese, and iron with WHO (2017) drinking water quality guideline and NDWQS (2022)

Parameters	NDWQS (2022)	WHO (2017)	Exceeding NDWQS (2022) (%)	Exceeding WHO (2017) (%)
Fe (mg/L)	0.30	NA	28.9	NA
Mn (mg/L)	0.20	NA	55.6	NA
As (mg/L)	0.050	0.010	20.0	71.2

NA: Not applicable

Relationships of monitored physicochemical parameters

The relationships of the monitored physicochemical parameters in the groundwater wells is presented in Fig. 2. Arsenic has strong positive correlations with iron (r=0.47) and manganese (r=0.38) at $p<0.01$. The increase in concentration of arsenic in the groundwater wells is accompanied by iron and manganese. Manganese has a negative correlation with ORP (r=-0.32, $p<0.05$). It clearly indicates the precipitation of manganese oxides in oxidizing groundwater environment. Though the p-value is greater than 0.05, pH has positive correlation with arsenic (r=0.27). It signifies arsenic dissolution is favorable at high pH. Some earlier studies also showed similar results (Katsoyiannis and Katsoyiannis, 2006; Chapagain et al., 2009; Barzegar et al., 2015; Rodrigues et al., 2016). Smedley et al. (2002) demonstrated a positive correlation between arsenic in groundwater and pH, suggesting the potential influence of pH on arsenic mobilization. This finding is supported by Cheng et al. (2009), who indicated that increased pH favors arsenic mobilization. Arsenate adsorption onto iron and manganese oxides is less effective when the pH is elevated (Dzombak and Morel, 1991; Edwards, 1994; Helena et al., 1999), which leads to the mobilization of arsenic in groundwater.

There are positive correlations of arsenic with iron and manganese. The Fe/Mn oxy-hydroxide mechanism is responsible for the elevated level of arsenic under reducing condition (McArthur et al., 2004; Smedley and Kinniburgh, 2013; Yadav et al., 2015). Reducing environment is responsible for the release of iron and manganese through the reduction of Mn (III, IV) (hydr)oxides to soluble Mn (II) and of Fe (III) (hydr)oxides to soluble Fe (II), respectively, and consequently, reduction of Mn (III, IV) (hydr)oxides and Fe(III) (hydr)oxides result in the release of arsenic adsorbed in Fe/Mn oxyhydroxides (McArthur et al., 2004). Furthermore, in the oxygenated zone, arsenic (V) is stable, and in anoxic conditions arsenic (III) is stable (Edwards, 1994; Lu and Zhu, 2011). Arsenic can absorb on or co-precipitate with iron and manganese and adsorb onto clay mineral surfaces under oxidative conditions (Pierce and Moore, 1982; Kim et al., 2002; Foster, 2003) and in reducing environment dissolution of these metals result in a higher concentration of the metals in groundwater (Smedley and Kinniburgh, 2013; Ni et al., 2016).

Iron and manganese oxy-hydroxide precipitation and its ability to absorb metals are the major controlling factors that lead to metal concentration in groundwater wells (Saha and Sinha, 2018). This may exhibit the influence of similar geochemical processes and the hydrodynamic behavior of iron and manganese in groundwater wells (Dragon and Gorski, 2015). Arsenic mobilization is high in the reducing condition due to Fe/Mn oxides and the direct reduction of arsenic (V) into arsenic (III). Fine sediments and organic materials are deposited in the inter-fan lowlands of the Terai region of Nepal (Sharma, 1995; McArthur et al., 2004; Shrestha et al., 2018). So, the higher arsenic concentration might be associated with the geological setup (fine-grained sediments) in the Rajpur Municipality.

Arsenic vs depth of groundwater wells

Though the p-value is >0.05, the correlation analysis exhibits r=-0.09, evidencing a slight negative correlation between arsenic and the depth of the groundwater wells (Fig.3). Therefore, arsenic concentration varied with the depth of groundwater wells.

The slight negative correlation between arsenic and the depth of the groundwater wells might be attributed to an increase in the water table that results in the groundwater table being closer to the land surface and the mixing of the groundwater with wastes including agrochemical wastes at the surface or nearby surface of the water (Yadav et al., 2015). The dissolution of Fe-oxyhydroxide may be triggered by the rise in the water table as flood plain sediment gets buried and favors the release of arsenic under a reducing groundwater environment (Nickson et al., 2000; Bhattacharya et al., 2001; Mueller, 2017). Furthermore, the water table goes down in the dry season and the nearby rivers which were mostly fed by the groundwater are likely to get dried up. This process enhances the leaching of arsenic-bearing minerals into the groundwater by river deposition (Yadav et al., 2015). Mueller (2017) also indicated that groundwater wells of a depth of fewer than 20 m observed higher arsenic concentration in the Terai region of Nepal. The difference in the redox environment which is assisted by ORP levels in the groundwater wells may be related to the depth-wise variation of arsenic as reductive dissolution is favorable for arsenic release. Though arsenic mobilization is favorable in the reducing environment in deep groundwater wells, the groundwater wells closer to land surface i.e., shallow groundwater wells tend to occur a higher concentration of arsenic which shows there is the possibility of influence of anthropogenic activities in the groundwater wells of the Rajpur Municipality.

Distribution of physicochemical parameters

Fig. 4 to 8 illustrate the distribution of physicochemical parameters in the study area. The higher concentration of arsenic was >0.100 mg/L in ward 1 (Pipra Bhagwanpur), while in ward 8 (Baluwa) it was <0.010 mg/L (Fig. 4). The higher concentration of iron (>6.0 mg/L) was in ward 1. The higher concentration of manganese (>1.00 mg/L) was observed in wards 1 and 2 (Phatuwa Maheshpur). The higher ORP (>100 mV) were in wards 8 and 9 (Bairiya) and a minimum of <-100 mV in the remaining wards. In addition, the EC was >1500 µS/cm in wards 5 (Rajpur Farhadwa) and 8. Similarly, wards 2, 5, 6 (Kudiya), and 7 (Akolwa) demostrated high EC as compared to the remaining wards of the Rajpur Municipality. Higher concentration of arsenic (0.010 to >0.100 mg/L), iron (0.3 to >6.0 mg/L), and manganese (0.20 to >1.00 mg/L) were in the

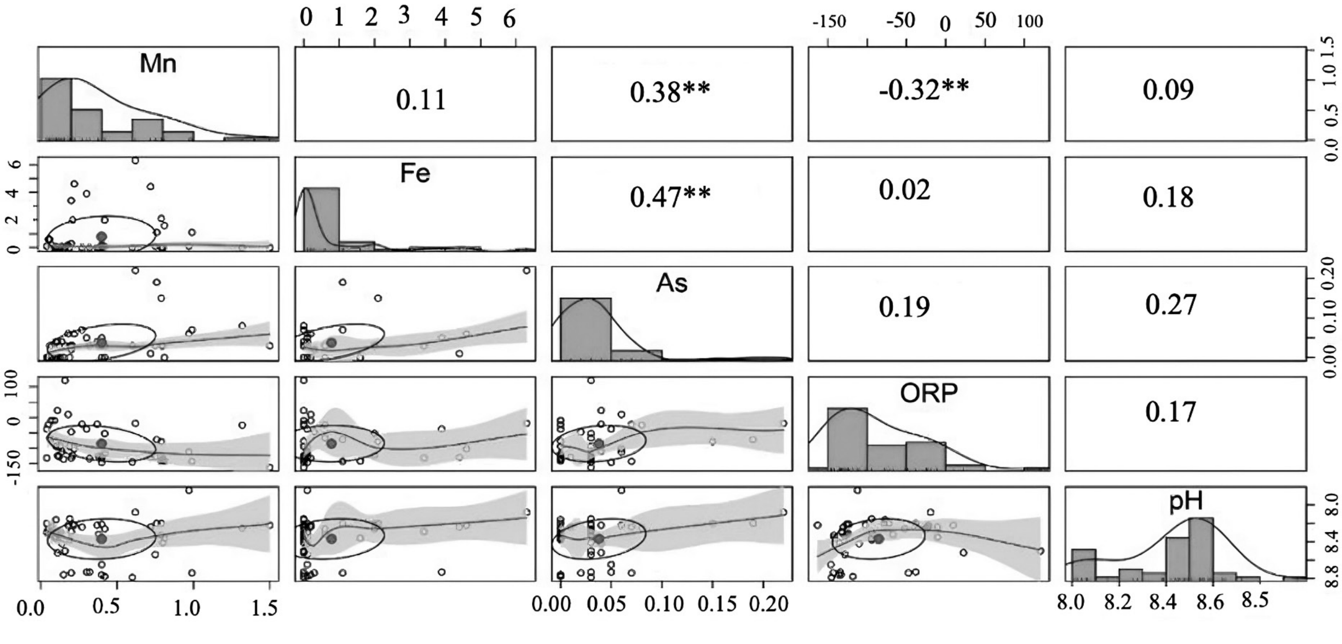

Fig. 2: Spearman's rank correlation coefficient in groundwater wells (n=45).

wards 1, 2, and 5. The higher concentration of manganese was in seven wards except in wards 4 (Rajpur Farhadwa) and 5. Paudyal (2011) suggested that gray micaceous fine sands, quartz, feldspar, muscovite, biotite, and brown rock fragments increase arsenic concentration. So, arsenic concentration in the groundwater wells of the Rajpur Municipality could be influenced by these minerals as well. A higher concentration of iron was observed in two wards (wards 1 and 7) and lower in the remaining wards. This indicates that the area could have contained pyrite minerals and rocks having low values of arsenic like ferrihydrite, hematite, lepidocrocite, goethite, magnetite, and Mg-ferrite (Diwakar, 2017).

The distribution patterns illustrate elevated EC, iron, manganese, and arsenic in many groundwater wells, indicating high mineralization. This depicts high mineralization in the groundwater wells, evidencing high mobilization of metals (Zheng et al., 2017). Furthermore, many groundwater wells exhibited low ORP, which is attributed to the mobilization of iron, manganese, and arsenic in the reducing environment. The groundwater wells with high mineralization might be attributed to geochemical heterogeneity of the sediment in the Rajpur Municipality, where there is a presence of finer particles in the sediments (Sharma, 1995; Shrestha et al., 2018). Besides, the decrease in sediment grain size tends to increase the concentration of metals (Filipek and Owen, 1979; Singh et al., 1999; Gurung et al., 2007; Pathak et al., 2009). Fine sediments have a higher surface area than coarser sediments and are more reactive (Waychunas et al., 2005). Nevertheless, many monitored groundwater wells exhibited low ORP

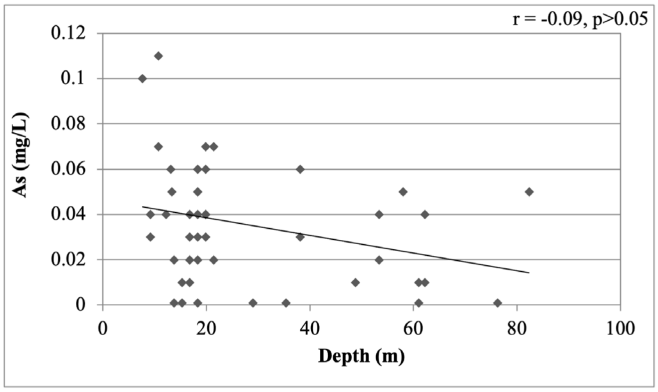

Fig. 3: Scatter plot of depth and arsenic.

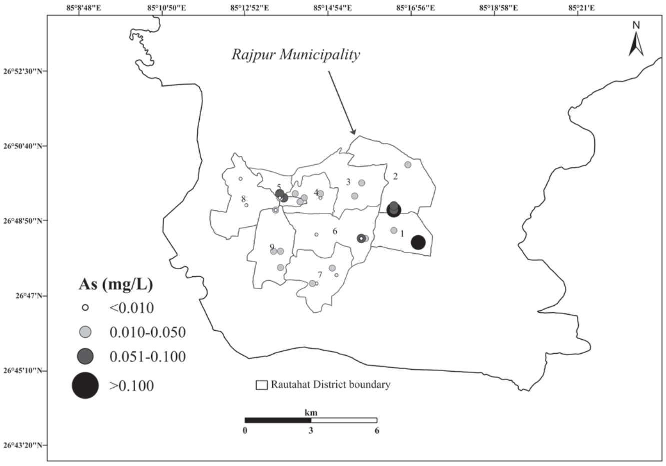

Fig. 4: Distribution of arsenic.

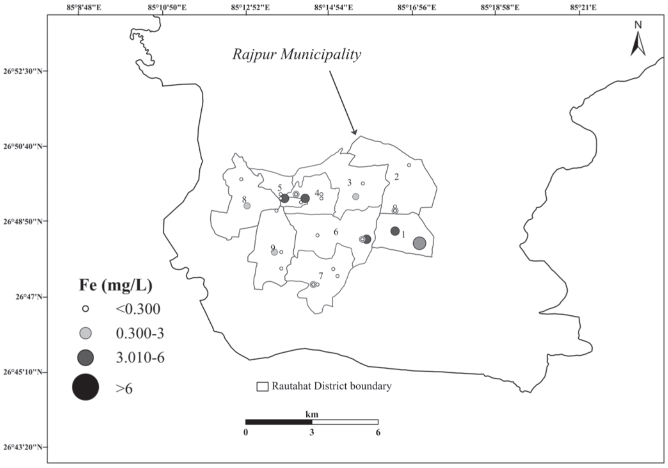

Fig. 5: Distribution of iron.

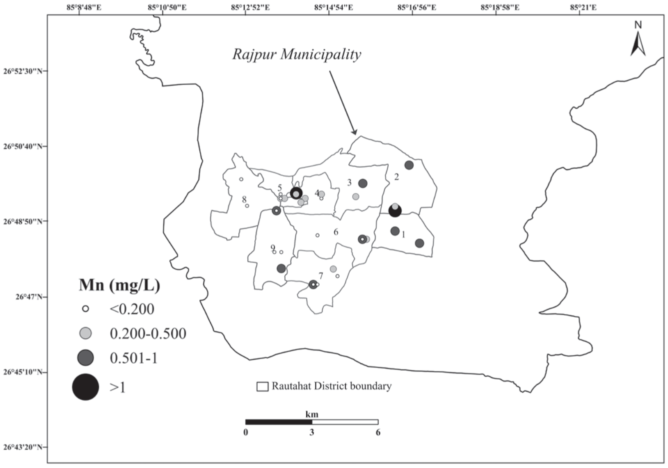

Fig. 6: Distribution of manganese.

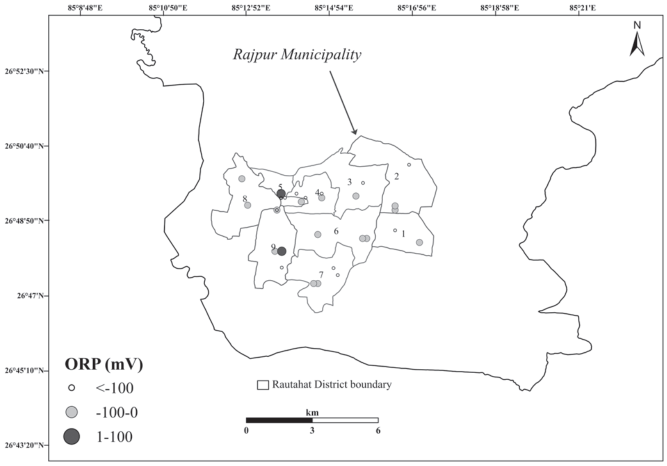

Fig. 7: Distribution of ORP.

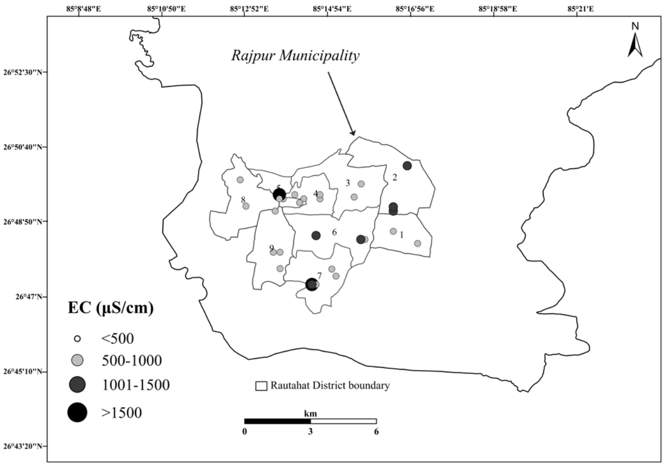

Fig. 8: Distribution of EC.

value, indicating a reduced groundwater environment, which enhances mineral mobilization causing high mineralization in groundwater wells (Mukherjee et al., 2012).

Influential physicochemical parameters in the groundwater

The PCA is presented in Table 4. In the first PC, 36.22% of the total variance is contributed by the high loading factor of pH and considerable loading factor of arsenic. The second PC accounting for 23.98% of the total variance is contributed by high loading factors of iron and arsenic and moderate loading factors of manganese. The third PC contributing to 18.56% of the total variance is attributed to the high positive loading factor of ORP and high negative loading factor of manganese.

Table 4: Loading of variables on significant principal components

Variables	PC1	PC2	PC3
Mn	0.308	0.462	**-0.694**
Fe	0.109	**0.778**	0.240
As	0.459	**0.731**	0.105
ORP	0.283	-0.102	**0.815**
pH	**0.613**	0.179	0.224
Eigen value	2.25	1.67	1.29
% of variance	36.21	23.98	18.56
% Cumulative variance	32.22	56.20	74.76

The PCA also indicates that arsenic mobilization is favorable in high pH values in the groundwater wells. In addition, iron, arsenic, and manganese are correlated. The clustering of these variables demonstrates a common origin for these metals likely from the dissolution and weathering processes of the minerals. The Fe/Mn oxyhydroxides are the common host matter for arsenic, either adsorbed into the surface or co-precipitated and the reductive process is responsible for arsenic mobilization by dissolution or desorption in the groundwater (McArthur et al., 2004; Liu and Wu, 2019). The observed result complies with the fact that manganese, arsenic, and iron become solid and never dissolve in water under highly oxidized conditions and vice-versa (Foster, 2003; Lu and Zhu, 2011). Furthermore, a low concentration of manganese is evident in the oxidizing groundwater environment, which could be due to precipitation of manganese as oxides in oxidizing environment.

CONCLUSION

The study has confirmed the occurrence of elevated concentrations of iron, manganese, and arsenic in the groundwater resources of the Rajpur Municipality. Iron concentration in nearly 29% of the samples in the groundwater wells exceeded the maximum concentration limit (0.3 mg/L) of NDWQS (2022). Manganese concentration in nearly 56% of the samples exceeded the maximum concentration limit (0.20 mg/L) of NDWQS (2022).

This study revealed that there is a wide variation of arsenic concentration that ranged from BDL to 0.220 mg/L. Arsenic concentration in about 71% of the samples exceeded WHO (2017) guideline value for drinking water of 0.010 mg/L and about 20% of the samples exceeded the maximum concentration limit (0.050 mg/L) of NDWQS (2022). Many groundwater wells exhibited low ORP, which is responsible for the mobilization of iron, manganese, and arsenic. The slight negative correlation between arsenic and depth of the groundwater wells indicates that shallow groundwater wells (<50 m) exhibits elevated levels of arsenic in comparison with deep groundwater wells.

The PCA demonstrates that iron, manganese, and arsenic in the groundwater are from a common natural origin likely through the reduction of Fe/Mn oxyhydroxides. Therefore, Fe/Mn oxyhydroxide precipitation and its ability to adsorb metals are the major controlling factors that lead to heavy metal concentration in the groundwater. Nevertheless, comprehensive investigations are necessary to elucidate the mechanisms of heavy metal contamination in the groundwater from sources such as industrial effluents, sewage, pesticides, herbicides, and fertilizers. The elevated levels of iron, manganese, and arsenic in the groundwater wells of the Rajpur Municipality indicate the need for proper management of groundwater resources in the municipality. Filtration using activated alumina or iron-based media, reverse osmosis, or adsorption could be helpful to reduce the arsenic content from the groundwater used for human consumption. Furthermore, public awareness programs and involvement of health-related organizations in the vulnerable areas (e.g., Pipra Bhagwanpur) could be effective strategies to minimize the problems caused by arsenic in the groundwater.

AUTHOR'S CONTRIBUTIONS

Md. Asif Alam and Kiran Mishra contributed in field work, laboratory work, and manuscript preparation. Suman Man Shrestha was involved in conceptualization, supervision, manuscript preparation, and writing review and editing. Satyam Kumar Chaudhari assisted in manuscript writing.

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