Environ Geochem Health (2020) 42:1905–1920
https://doi.org/10.1007/s10653-019-00457-6

ORIGINAL RESEARCH

Assessment of soil and groundwater contamination at a former Tannery district in Dhaka, Bangladesh

Md Shahin Alam · Bangshuai Han · Al-Mizan · John Pichtel

Received: 17 May 2019 / Accepted: 25 October 2019 / Published online: 7 November 2019

Abstract The uncontrolled and unplanned development of leather processing industries in Bangladesh has contaminated land and water, prompting concerns for public health. Hazaribagh, located in the southwestern part of Dhaka, has been the city's principal leather processing zone since the 1960s. In order to alleviate the environmental contamination and public health risks to citizens of Hazaribagh and downstream, a relocation project was launched to remove the tanning industry. However, soil and groundwater quality conditions of the former industrial sites must be assessed and/or remediated for commercial and residential use. Soil was collected from ten sites and tested for concentrations of potentially toxic metals (Pb, Cr, Zn, Cu, Ni and Cd), and groundwater was collected from six sites and analyzed for physiochemical parameters and potentially toxic metals. Concentrations of soil Cr, Zn and Cu exceeded the European Union maximum permissible concentrations. Deep groundwater Cr concentration in one location exceeded the Bangladesh DoE maximum limits; however, deep groundwater is overall of good-to-excellent quality. Spatial variations of soil and groundwater contamination in Hazaribagh indicate that contaminants have not spread laterally. Based on local conditions, current technologies, contamination level, time and cost, and ease of operation, it is suggested that soil flushing, electrokinetics and/or phytoremediation could be options for remediation of affected soil and groundwater in the Hazaribagh district.

Keywords Groundwater · Soil · Contamination · Tannery · Metal · Public health · Hazaribagh · Chromium

Introduction

The city of Dhaka, with a population of over 12 million, is the heart of business, industry and government in Bangladesh (Fig. 1). Leather processing (i.e., tannery) industries have flourished in the Hazaribagh area in southwestern Dhaka since the mid-1960s (Hossain 2008; Karn and Harada 2001). This industrial zone has been gradually expanding; 95% of Bangladesh tanneries consider Hazaribagh the city's principal leather processing zone (Huq 1998). In 2016–2017, total income from leather, footwear and manufactured leather goods in Hazaribagh was $1.39 billion, comprising 4% of the country's GDP (Aggarwal et al. 2009).

M. S. Alam · B. Han (✉) · J. Pichtel
Ball State University, Environment, Geology and Natural Resources, Muncie, IN 47306, USA
e-mail: bhan@bsu.edu

Al-Mizan
Leather Engineering, Khulna University of Engineering and Technology (KUET), Khulna 9203, Bangladesh

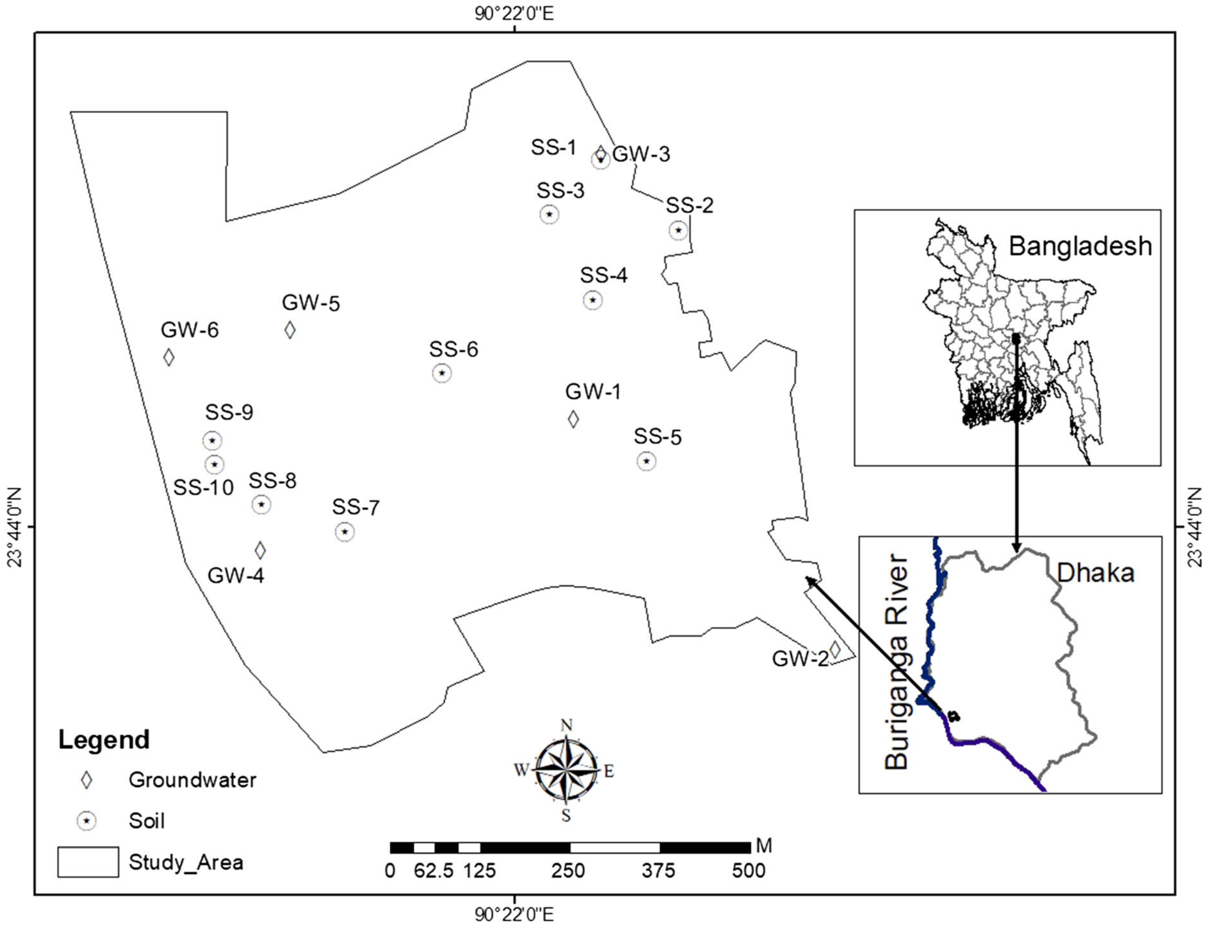

Fig. 1 Spatial distribution of soil and groundwater sampling sites in Hazaribagh, and the location of the study area in Bangladesh

Although the tannery sector contributes significantly to the Bangladesh economy, uncontrolled and unplanned expansion of the industrial zone has affected the local environment. During the tanning process, animal skin is treated to eliminate flesh, fat, hair and other unwanted substances using various chemicals and then treated with trivalent chromium (Cr^{3+}) or tannins, mineral salts and colors to produce leather. The resulting tannery effluents are often enriched with substantial quantities of metals and other toxic contaminants. For example, basic chromium sulfate is a commonly used tanning agent that results in wastewater with Cr concentrations ranging from 500 to 3000 mg/L (Aravindhan et al. 2004). Although Cr in tanning industry often occurs in the trivalent form, it is commonly converted to the more toxic hexavalent form (Cr^{6+}) in the discharge (Alvarez-Bernal et al. 2006). Ingestion of Cr^{6+} is associated with cancer, renal damage, allergies and asthma in humans (Jacobs and Testa 2005; Gebrekidan et al. 2013). Cadmium (Cd) and lead (Pb) are widely used as pigments in the leather industry as they impart vibrant colors. For example, cadmium sulfide is used as a yellow pigment and cadmium selenide as a red pigment. Ingestion of Cd is linked with cardiovascular, kidney, nervous system and bone diseases (Tchounwou et al. 2012), and Pb damages the peripheral and central nervous systems as well as other organ systems (Tchounwou et al. 2012). A range of other noxious and toxic chemicals, e.g., ammonium salts, sulfides, chlorobenzene, formic acid, sodium hypochlorite, sodium hydroxide and sulfuric acid, are also used in various leather making and tanning processes (Shakir et al. 2012).

Recovery of metals during tanning suffers from drawbacks such as generation of toxic solid wastes, high capital and operational costs, and post-treatment effects due to incomplete treatment of wastewater (Maier et al. 2004). Contaminant removal from tannery effluents has, therefore, been poorly conducted in many less developed countries, especially those lacking comprehensive environmental regulations. Over seven decades, effluents from tannery industries have been discharged directly into soil and surface water bodies of Hazaribagh.

Tannery effluents contain substantial solid wastes including leather fragments and animal fat, flesh, and hair, etc., which had previously been stockpiled on tannery properties. Prior to 1988, the lowlands of Hazaribagh were regularly flooded by the nearby Buriganga River (Fig. 1), which consequently dislocated tannery wastes. Following severe flooding in 1988, the Dhaka Protection Embankment, which occurs adjacent to the river, was raised. As a result, wastes were no longer lost in runoff; however, a substantial amount of waste was subsequently dumped in surrounding residential areas, creating episodes of severe contamination during the monsoon season (Hashem et al. 2015).

The discharge of tannery effluents and associated toxic compounds into aquatic systems poses significant public health and environmental concerns. Approximately two million people living in proximity to Hazaribagh and the Buriganga River are affected by tannery wastes (Arias-Barreiro et al. 2010). Metal and other chemicals may pollute the soil, leach into the water table and contaminate irrigation and drinking water, and thus adversely affect the quality of drinking water and crop products (Namaghi et al. 2011). Furthermore, aquatic ecosystems will be impacted; the aquatic life of the Buriganga River has declined in quality in recent decades (Ahmad et al. 2010). Although many factors (e.g., soil texture, pH, and organic content) affect the mobility of metals, Cr generally has high mobility than Cd and Ni, and Pb has little mobility under common conditions based on column leaching experiments (Dong et al. 2009; Sherene 2010). As such, Cr likely exhibits greater mobility in soil and is more likely to reach groundwater if soil is contaminated.

Due to the significant health and environmental concerns raised by tannery industries in Hazaribagh, a relocation plan was formulated (Bhowmik 2013). All tanneries were required to move to an industrial area in Dhaka by 2017. New commercial and residential construction is being planned for the Hazaribagh area. However, soil and groundwater continue to suffer from existing contaminants including the presence of tannery wastes (Halim et al. 2011).

There is an urgent need for assessment of soil and groundwater conditions in Hazaribagh; furthermore, feasible technologies for remediation must be instituted. Limited empirical studies have addressed the impact of tannery wastes on soil and groundwater quality in Bangladesh; likewise, proposed methods to clean affected sites have been limited (Juel et al. 2016). The choice of the most appropriate soil and groundwater remediation technique(s) relies upon site attributes, types and amounts of contaminants, and future use of the site (Halim et al. 2011). In this study, we assess soil and groundwater conditions in the Hazaribagh district of Dhaka and offer suggestions on remediation technologies that are most suitable based on local conditions.

Experimental methods

Site description

Dhaka, capital city of Bangladesh, is located at 23° 46′ 38″ N and 90° 23′ 58″ and has a total area of 306 km^2 (Fig. 1). Elevation is 22 m above sea level. With a total population of over 12 million, Dhaka is ranked as the 11th largest city in the world. Dhaka is located to the east of the Buriganga River which flows into the Bay of Bengal. Climate is tropical with a distinct monsoon season. Monthly average temperature ranges from 19 °C in January to 29 °C in June. Average annual rainfall is about 2148 mm, ranging from 8 mm in January to 373 mm in July (Bangladesh Meteorological Department 2019).

Hazaribagh measures approximately 0.55 km^2 and is located on the southwest side of Dhaka, along the Buriganga River (Fig. 1). Soil of the Hazaribagh area is calcareous saline alluvium with a silt loam texture, poorly to very poorly drained, and seasonally flooded (Mondol et al. 2017). The upper layer of the aquifer is semi-confined, extending down to 20–30 m from the ground surface (FAO 1988). Subsurface materials gradually shift to fine sand (15–30 m thick) and then medium to coarse sand in deeper areas, forming an aquifer with relatively high hydraulic conductivity (about 11–18 m/day) (Halim et al. 2011).

Data collection

Soil samples were collected from ten locations in Hazaribagh. The site coordinates were recorded using GPS and were randomly selected from locations having exposed soil (unpaved). All samples (Fig. 1) were collected from 10 to 50 cm depth and placed into airtight polyethylene bags. Soil samples were transported to the Environmental Laboratory of the Civil Engineering Department, Bangladesh University of Engineering and Technology, where they were split into two subsamples each. One subsample was used for determination of pH following ASTM D4972 using a potentiometer with a pH-sensitive electrode system (ASTM D4972-13 2013) and electrical conductivity (EC) following Rayment and Higginson (1992). The other sample was used for determination of metal concentrations (Pb, Cr, Zn, Cu, Ni and Cd).

Soil samples for metal tests were first homogenized and dried in an oven. Then, 5 g of each sample after being dried was digested in a 1:3 mixture of HNO_3/HCl at 100 °C for 24 h. Solutions were filtered through 0.45-µm pore size membrane filters. Filtrates were analyzed via flame atomic absorption spectrophotometry (FAAS) using an air/acetylene mixture (Shimadzu AA 6800). The instrument was linearly calibrated with standards before each analysis and was checked with standards again after analysis. All tests were performed three times for each sample, and the mean values and standard deviation were reported. Metal concentrations were compared with European Union (EU) maximum permissible concentrations (MPC).

Groundwater samples were collected from municipal water supply wells and private wells in Hazaribagh at depths ranging from 232 m to 320 m. Shallow groundwater contamination in the area has been reported from previous research, while deep groundwater condition is still unknown (Zahid et al. 2006). Groundwater samples were placed into pre-cleaned 1-L polyethylene bottles. The filled bottles were immediately placed in an ice-filled cooler and transported to the laboratory. Samples were stored at 4 °C, digested and analyzed within 72 h following USEPA method 3005A. Concentrations of Cr, Pb, Ni, Cu, Cd, Zn, Na, K, Ca and Mg were determined by FAAS. Other physiochemical variables were measured using the methods listed in Table 1. All tests were performed three times for each sample, and mean values were reported.

Data analysis

Soil and groundwater metal concentrations were compared to Bangladesh or EU MPC limits. In order to analyze the spatial variability of the contaminants throughout the area, soil and groundwater metal concentrations were interpolated using an inverse distance-weighted method (IDW) in ArcGIS.

To obtain a comprehensive understanding of overall groundwater quality, a variety of methods were employed to explore the groundwater physiochemical characteristics, including the Pearson's correlation coefficient matrix between different chemicals variables, the Piper diagram and the Water Quality Index (WQI).

The Pearson's correlation coefficient matrix between different chemical variables in the groundwater could indicate the relationship of physicochemical parameters in the study area and is a widely used method in groundwater physical chemical parameters analysis. The correlation matrix of 15 variables is calculated following Eq. 1 as below:

$$r = \sum \frac{(x - \bar{x})(y - \bar{y})}{\sqrt{\sum (x - \bar{x})^2 (y - \bar{y})^2}} \quad (1)$$

where x and y are variables, and x and y are mean values of all samples for each variable. The value of r ranges from − 1 to 1; $r = 1$ indicates the perfect positive linear correlation and $r = -1$ reveals perfect negative linear correlation.

Piper diagrams are used to show the relative abundance of the major ions from groundwater analyses (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, CO_3^{2-}, HCO_3^-) and produce a single point for each sample. These plots include two triangles, plotting cations and anions each. The cation and anion fields are combined to show a single point in a diamond-shaped field. Analysis could then be made based on the concept of hydro-geochemical facies (Chadha 1999). These tri-linear diagrams are useful in visualizing the similarities and differences of groundwater samples and analyzing the local overall geochemical characteristics.

Water Quality Index (WQI) is an efficient method for reflecting the composite influence of different

Table 1 Physicochemical parameter of groundwater samples with Bangladesh standards and WHO guidelines

Groundwater parameter	Instrument/procedure	Method
pH	Hach HQ30D pH meter	USEPA Method 8156
TDS	Oven, analytical balance	USEPA Method 160.1
EC	Hach HQ30D conductivity meter	Hach Method 8160
Sulfate	UV–visible spectrophotometry (Hach DR/6000)	USEPA Method 8051
Hardness	Titration with EDTA	Hach Method 8226
Carbonate/bicarbonate	Nomograph	USEPA Method 4500 B
Alkalinity	Titration	USEPA Method 310.1
Chloride	Potentiometric titration	USEPA Method 9212
Phosphate	Hach DR/2010	US EPA Method 8048
Ammoniacal nitrogen	Hach DR/2010	Hach Method 8038
Nitrate nitrogen	Hach DR-6000	Hach Method 10049
Nitrite nitrogen	Hach DR-6000	Hach Method 8507

water quality parameters on the overall water quality. Until recently, there has been an absence of a globally agreed composite index of water quality, partly because of the complexity of the water quality issues in specific areas (Tyagi et al. 2013). Nonetheless, various countries, including the USA, have relied on WQI to help transform information, help decision makers and assess the effectiveness of water quality management (Horton 1965; Harkins 1974; Cude 2001; Tyagi et al. 2013).

In this study, we adopted the WQI for drinking water developed by Batabyal and Chakraborty (2015) in India due to its physical approximation to the study area. Briefly, the WQI in Batabyal and Chakraborty (2015) is calculated following three steps. The first is to assign weight (w_i) to the measured water quality parameters according to their relative importance in the overall quality of water for drinking purposes. Weight ranges from 1 to 5 are provided, following Batabyal and Chakraborty (2015) (Table 2). Next, a relative weight (W_i) of the chemical parameter is calculated using the equation:

$$W_i = w_i / \sum_{i=1}^{n} w_i \tag{2}$$

where W_i is the relative weight of the ith parameter, w_i is the weight of each parameter and n is the number of parameters.

The third step is to calculate a quality rating (q_i) for each parameter based on the measurement and the standards according to Bangladesh or WHO guidelines, as below:

Table 2 Weight assigned to each parameter for WQI calculation

Parameter	Weight (w_i)	Relative weight (W_i) $W_i = w_i/\sum w_i$
pH	4	0.058
EC (µS/cm)	3	0.043
Alk (mg/L)	4	0.058
Hardness (mg/L)	2	0.029
TDS (mg/L)	4	0.058
Cl^- (mg/L)	3	0.043
HCO_3^- (mg/L)	3	0.043
NO_3-N (mg/L)	5	0.072
NO_2-N (mg/L)	5	0.072
SO_4^{2-} (mg/L)	4	0.058
Na^+ (mg/L)	2	0.029
K^+ (mg/L)	2	0.029
Ca^{2+} (mg/L)	2	0.029
Mg^{2+} (mg/L)	2	0.029
NH_4^+ (mg/L)	5	0.072
PO_4^{3-} (mg/L)	4	0.058
Cr (mg/L)	5	0.072
Zn (mg/L)	1	0.014
Cu (mg/L)	4	0.058
Ni (mg/L)	5	0.072
	69	1.000

$$q_i = \left({}^{C_i}/_{S_i} \right) \times 100\% \tag{3}$$

where q_i is the quality rating, C_i is the concentration of each chemical parameter in each water sample in mg/L and S_i is the guideline value as given in Bangladesh or WHO guidelines.

The WQI is calculated as the summation of each subindex (SI_i) which is determined for each chemical parameter:

$$\mathrm{SI}_i = W_i \times q_i \tag{4}$$

$$\mathrm{WQI} = \sum_{i=1}^{n} \mathrm{SI}_i \tag{5}$$

where SI_i is the subindex of ith parameter.

Water quality is then divided into four categories based on WQI range: (1) excellent water if < 50; (2) good water if 50–100; (3) poor water if 200–300; (4) very poor water if > 300.

Results

Pollutants in soil

In general, soil Cr, Cu and Zn concentrations were higher than those of Pb, Ni and Cd (Fig. 2, Table 3). Chromium had highest average and median concentrations (4105 mg/kg and 1026 mg/kg, respectively), with values in almost all samples exceeding the EU MPC (150 mg/kg) and typical background levels which was reported to range between 1.0 and 50 mg/kg (Islam et al. 2018). Median concentrations of Cu (122 mg/kg) and Zn (339 mg/kg) were close to the EU MPC (140 and 300 mg/kg for Cu and Zn, respectively). Specifically, Zinc concentrations at six locations exceeded the EU MPC, while Cu concentrations in four locations exceeded the EU MPC. Concentrations of Cd, Pb and Ni were well below the EU MPC or US Environmental Protection Agency (EPA) guidance. The Ni MPC was adopted from the US EPA as no EU limits are published. Soil Cd occurred in only trace concentrations, ranging from non-detectable to 0.16 mg/kg, which are substantially below the EU MPC (3 mg/kg). The range of Cr, Zn and Cu concentrations was greater than those for Pb, Ni and Cd. For example, the concentration of Cr ranged from a minimum of 114 mg/kg to a maximum of 15,520 mg/kg.

Soil metal concentrations exhibited different spatial distributions (Fig. 3). Lead concentrations varied between the northeast (NE) and southwest (SW) parts of the study area, with all samples below the EU MPC. All samples had high Cr concentrations, with highest levels located at the center to southeast (SE) (near SS5 and SS6). Zinc concentrations in samples SS1, SS2, SS9 and SS10 were above the EU MPC, while those from the central and southern parts were at or below the EU MPC. High Cu concentrations were observed mostly in the NE, with SS8 as an isolated high value in the SW. High Ni concentrations were mostly observed around the periphery of the study area (e.g., SS1, SS2, SS4 and SS10) and were generally below the EU MPC. Cadmium values tended to be low; however, high values were noted for samples in NE (i.e., SS2 and SS3). Five of the six metals (i.e., Pb, Zn, Cu, Ni

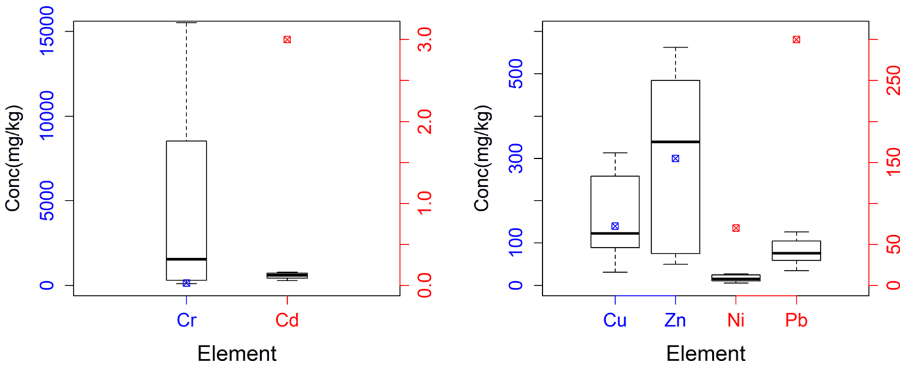

Fig. 2 Boxplots illustrating statistical distributions of concentrations of Cr, Cd, Cu, Zn, Ni and Pb in soil samples from Hazaribagh. The plot contains the median value (50 percentile), the first and third quantiles, as well as the maximum and minimum of the data. The EU MPC (US EPA MPC for Ni) is denoted as a point marker for each metal

Table 3 Metal concentrations of tested soil samples with mean and standard deviation

Sample	Pb	Cr	Zn	Cu	Ni	Cd
SS-1	54.20 ± 0.12	113.60 ± 0.77	483.90 ± 0.28	226.30 ± 0.09	12.80 ± 0.04	0.16 ± 0.07
SS-2	17.90 ± 0.10	1537.40 ± 0.42	562.50 ± 0.07	284.50 ± 0.10	10.60 ± 0.03	0.15 ± 0.09
SS-3	37.40 ± 0.42	8530.50 ± 1.10	49.60 ± 0.09	313.20 ± 0.12	6.80 ± 0.03	0.09 ± 0.02
SS-4	41.10 ± 0.77	152.30 ± 0.12	74.90 ± 0.12	120.40 ± 0.06	13.70 ± 0.02	0.12 ± 0.03
SS-5	30.40 ± 0.20	15,519.50 ± 1.20	360.90 ± 0.14	89.00 ± 0.07	7.04 ± 0.01	ND
SS-6	21.80 ± 0.07	9899.70 ± 1.20	317.10 ± 0.30	46.80 ± 0.05	3.04 ± 0.01	ND
SS-7	65.30 ± 0.10	515.10 ± 0.20	69.50 ± 0.07	124.50 ± 0.07	8.90 ± 0.01	0.13 ± 0.03
SS-8	64.60 ± 0.15	312.80 ± 0.30	76.80 ± 0.08	257.90 ± 0.14	5.70 ± 0.01	ND
SS-9	40.80 ± 0.09	4347.00 ± 0.42	435.70 ± 0.14	30.80 ± 0.07	3.60 ± 0.02	0.06 ± 0.01
SS-10	36.50 ± 0.07	122.80 ± 0.10	532.10 ± 0.20	94.70 ± 0.09	13.30 ± 0.05	ND

Unit: mg/kg

ND non-detectable

and Cd) exhibited higher concentrations in the NE. Overall, as many as three metals in the study area exceeded EU MPC standards in all soil samples of each site.

Pollutants in groundwater

The regulatory standards from the Bangladesh government and WHO, as well as instrument detection limits for each metal tested in groundwater, appear in Table 4. Lead and Cd were non-detectable (detection limit of 10 µg/L for both) in all groundwater samples (Table 4, Fig. 4). Concentrations of Cd, Cu, Ni, Pb and Zn were below hazardous levels. Concentrations of Cu, Ni and Zn were orders of magnitude below the Bangladeshi MPC. The concentration of Cr in groundwater was also mostly lower than the MPC level (10 µg/L), with only one sample, GW-2 (45.4 µg/L), exceeding it.

Metal concentrations exhibited varied spatial distribution in groundwater (Fig. 5). Chromium concentration was high in GW-2 which exceeded the Bangladesh MPC, but was low elsewhere. Despite the safe levels of Zn, Cu and Ni, concentrations still exhibited spatial differences. Specifically, Zn and Ni concentrations were highest in GW-5, while Cu concentration was higher in GW-4 and GW-6. Overall, metal concentrations in the study area did not exceed the MPC standards, except for Cr in GW-2.

The pH values of groundwater samples were mostly neutral, ranging from 6.6 to 7.5 (Table 5). Alkalinity ranged from 126 to 207 mg/L. The ions Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^- and SO_4^{2-} all met DoE- and WHO-published limits. GW-3 was observed to have comparatively higher concentrations of several ions compared to other samples. Chloride concentration was highest in GW-2 (53 mg/L) but still below the DoE upper limit of 150–600 mg/L and WHO limit of 200 mg/L. TDS ranged from 255 to 367 mg/L, which also satisfies the DoE MPC of 1000 mg/L. EC ranged from 372 to 545 µS/cm, and hardness from 110 to 230 mg/L. The hardness value is, overall, lower than the DoE permissible limit of 200–500 mg/L as $CaCO_3$.

Discussion

Metal pollutants in soil and groundwater

Metal concentrations in topsoil and groundwater indicate that tanning industries have polluted soils and have affected drinking water sources. Chromium, Zn and Cu concentrations were higher than those of other metals in soil. In deep groundwater, Cr was also of concern due to high concentration, whereas all other metals occurred at relatively low concentrations. The maintenance of good water quality in the deep groundwater aquifer was likely due to the presence

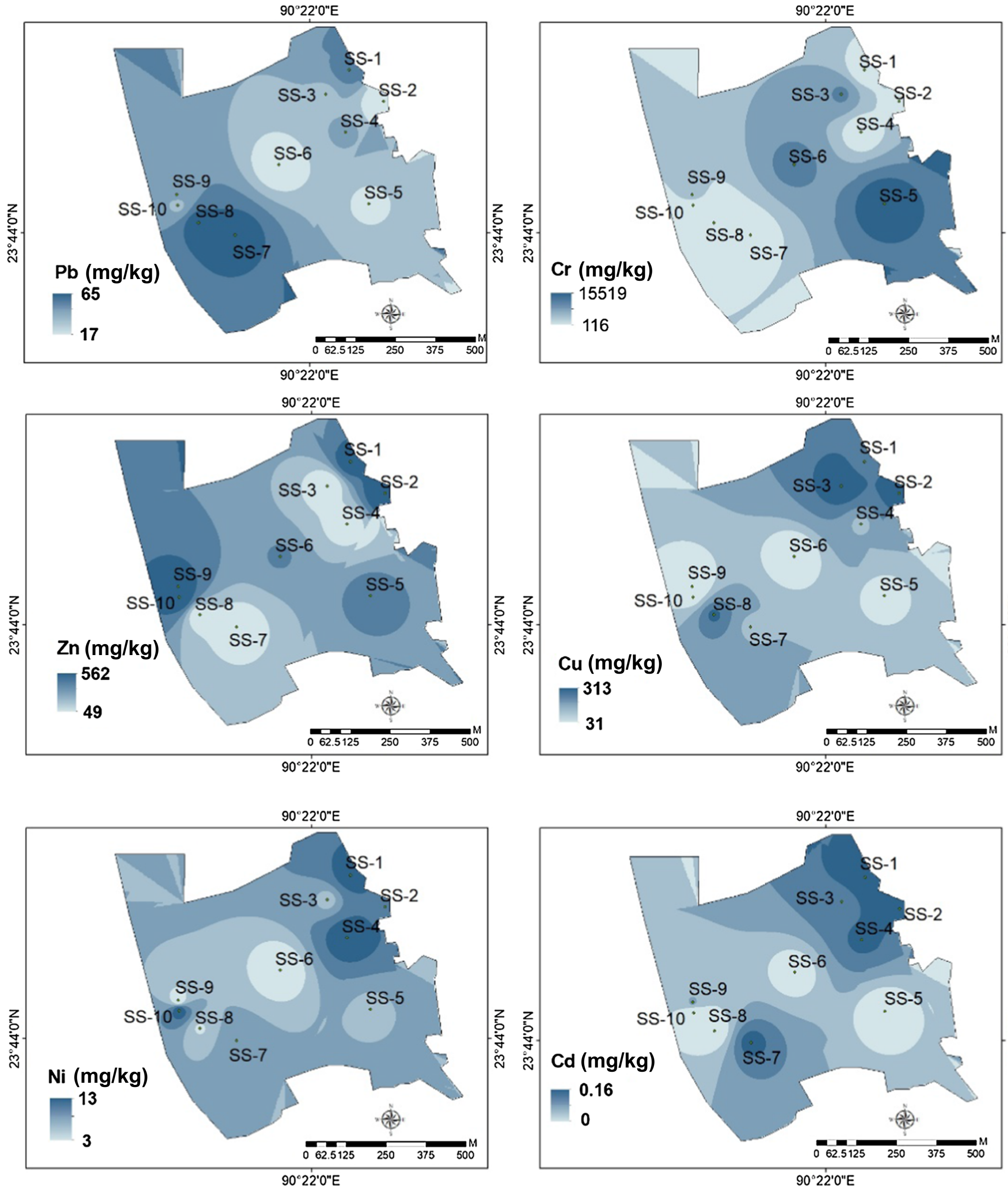

Fig. 3 Spatial distribution of metal concentration in the soil of Hazaribagh. The spatial distribution is interpolated from the point sample values using inverse distance method in ArcGIS

of a thick layer of clay and silt semi-aquiclude above the unconfined aquifer (Halim et al. 2011), which may adsorb and accumulate metal ions and thus protect groundwater. However, once contaminated, remediation of contaminants in deep groundwater aquifers can be extremely challenging. One of the deep

Table 4 Metal concentration of groundwater samples with Bangladesh standards, WHO guidelines and instrumental detection limit

Samples	Pb (µg/L)	Cr (µg/L)	Zn (µg/L)	Cu (µg/L)	Ni (µg/L)	Cd (µg/L)
GW-1	ND	2.000 ± 0.037	41.000 ± 0.131	3.000 ± 0.021	2.000 ± 0.013	ND
GW-2	ND	45.000 ± 0.883	33.000 ± 0.191	ND	4.000 ± 0.032	ND
GW-3	ND	3.000 ± 0.026	ND	1.000 ± 0.110	4.000 ± 0.026	ND
GW-4	ND	3.000 ± 0.234	43.000 ± 0.230	14.000 ± 0.011	2.000 ± 0.019	ND
GW-5	ND	7.000 ± 0.208	47.000 ± 0.110	3.000 ± 0.100	6.000 ± 0.110	ND
GW-6	ND	4.000 ± 0.172	39.000 ± 0.013	13.000 ± 0.020	4.000 ± 0.030	ND
Guidelines						
Bangladesh	50	50	5000	1000	100	5
WHO	10	50	3000	0–2000	20	5
Detection limit	10	1	1	1	10	1

ND non-detectable

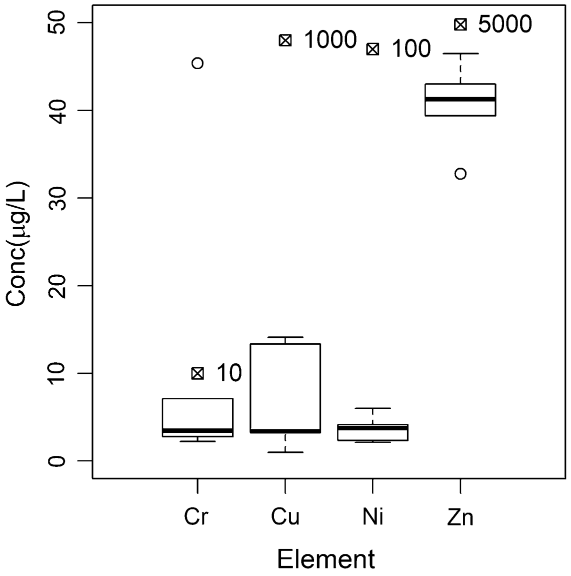

Fig. 4 Boxplots illustrating statistical distributions of concentrations of Cr, Cu, Zn and Ni in groundwater samples from Hazaribagh. Pb and Cd are both undetectable and are not shown in the figure. The MPC set by DoE, Bangladesh, is denoted with point makers in the figure. Note that some MPC values are not of the same scale with groundwater observations so MPC values are provided along with the markers

groundwater wells appears to have received Cr contamination from industrial activity due to its elevated concentration relative to other locations, which indicates that pollutants may continue to percolate to deep groundwater in Hazaribagh. This contamination fact may have long-lasting influences on human health since groundwater is the major drinking water source in Dhaka. Halim et al. (2011) found that shallow groundwater in Hazaribagh was contaminated by Pb and Cd from tanning industries. The current study reveals that Pb and Cd contaminants do not yet occur in deep groundwater. Chromium, especially in hexavalent form, is less adsorbed to soil particles and has higher mobility in soil than Cd and Pb and may reach groundwater faster (Dong et al. 2009; Sherene 2010). In contrast, Pb, Cd and Ni attach to soil colloids and are immobilized unless the soil is acidic (Wuana and Okieimen 2011). In addition, Cr is expected to be in the greatest relative abundance, given that it is used heavily in the tanning process. Considering the heavy use of Cr in local tanneries, the higher permeability and hydraulic conductivity of lower aquifers in the region (Halim et al. 2011), the potential health effects, along with the fact that the GW-2 has been contaminated by Cr, special attention should be paid to Cr in deep groundwater immediately.

Physicochemical groundwater parameters analysis

Physicochemical tests indicate that deep groundwater in the study area is generally in compliance with regulatory standards and is appropriate for beneficial use (Table 3). Groundwater pH values ranged from 6.6 to 7.0, which are consistent with values from Halim et al. (2011) for shallow groundwater of the region. The slightly acidic to neutral pH values might be due to the presence of local carbonate-rich rocks

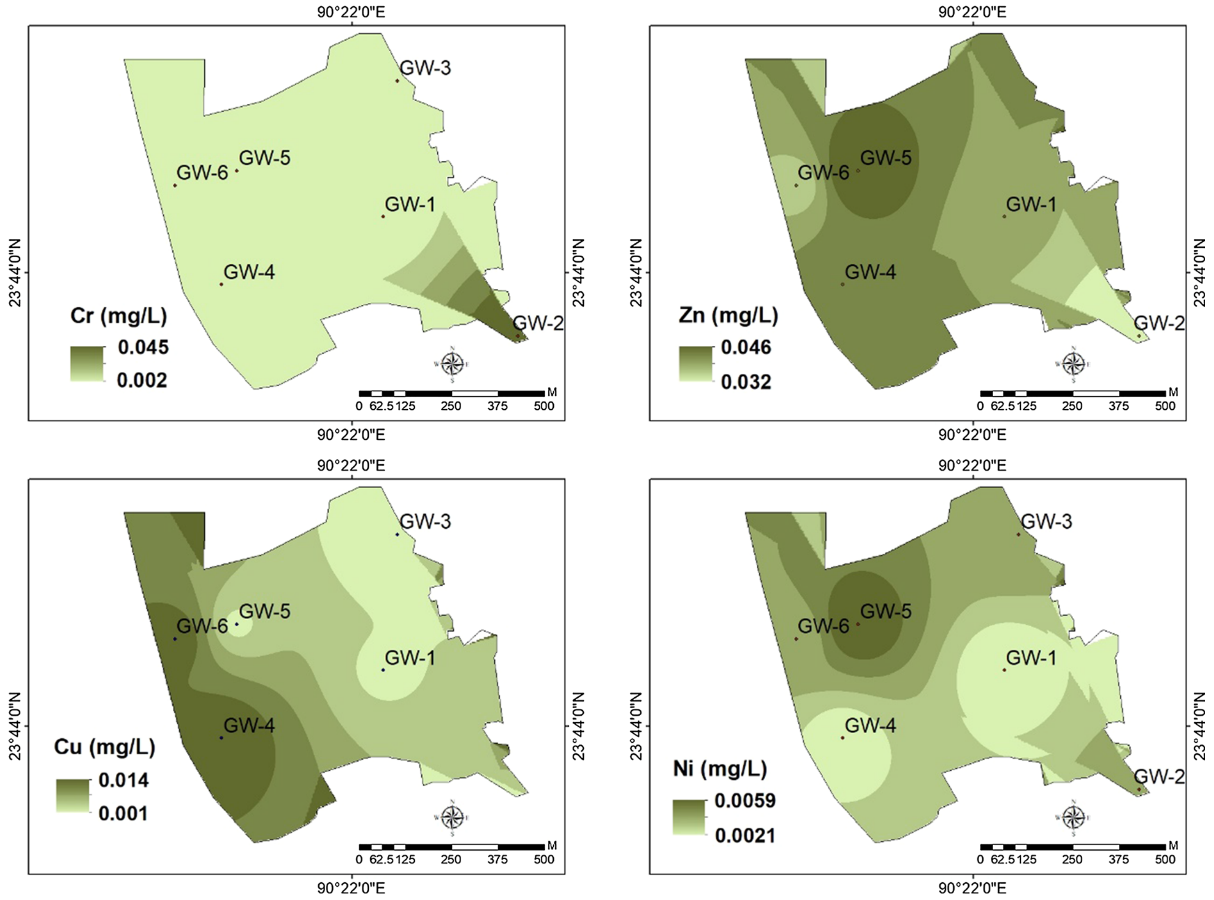

Fig. 5 Spatial distribution of metal concentration in the groundwater of Hazaribagh. The spatial distribution is interpolated from the point sample values using inverse distance method in ArcGIS

(Halim et al. 2011). The GW-2 well had the lowest pH value, i.e., 6.6, along with highest Cr, K and Cl concentrations, which may indicate that deep groundwater at GW-2 has been affected by use of potassium dichromate and other tannery-related salts.

The relative abundance of major cation concentrations (mg/L) in the deep groundwater was $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+} > NH_4^{+}$, while that of the anions was $Cl^{-} > SO_4^{2-} > NO_3^{-} > PO_4^{3-} > NO_2^{-}$. According to Zahid et al. (2006), Cl^{-}, NO_3-N, NO_2-N, SO_4^{2-} and PO_4^{3-} are within a safe range for drinking and irrigation purposes. Water hardness was mostly lower than the Bangladesh suggested range; however, moderately hard or soft water is not known to have negative effects to human health. Hardness may originate from local tanning and steel industries as well as dissolution of aquifer materials containing Ca^{2+} and Mg^{2+}.

It is likely that some Na^{+} and Cl^{-} originated from tanning industries. Chloride concentrations were consistent with previous research which showed Cl^{-} values of 62 mg/L (Zahid et al. 2006). Alkalinity values ranged from 126 to 207 mg/L as $CaCO_3$. No suggested limits have been established for alkalinity levels in drinking water worldwide; however, some alkalinity may be desirable in groundwater because of its importance in buffering pH change and thus maintaining groundwater quality. TDS values ranged from 255 to 367 mg/L and were all within safe levels.

From the correlation coefficient matrix (Table 6), a strong positive correlation ($r > 0.7$) was found between hardness and EC, TDS, Na^{+}, Ca^{2+} and Mg^{2+}. Hardness may originate from natural sources of rock dissolution, as well as the tanning industries which uses lime for removing hair and cleaning. More dissolved ions will lead to higher TDS and EC. A

Table 5 Physicochemical parameters of groundwater samples with Bangladesh standards and WHO guidelines

Parameter	GW-1	GW-2	GW-3	GW-4	GW-5	GW-6	Standards/guidelines	
							Bangladesh	WHO
Depth (m)	320	296	232	259	290	296	–	–
pH	7.1	6.6	7.5	6.9	7.4	7.0	7.0–8.5	6.5–8.5
EC (µS/cm)	432	500	545	372	502	475	–	–
Alk (mg/L)	126	168	192	184	197	207	–	–
Hardness (mg/L)	152	168	224	110	230	198	200–500	–
TDS (mg/L)	288	340	367	255	295	310	1000	500
Cl^- (mg/L)	47	53	50	11	42	25	150–600	250
NO_3-N (mg/L)	0.3	1.0	0.2	0.6	0.7	0.5	10	0.45
NO_2-N (mg/L)	0.002	0.003	0.002	0.003	0.004	0.004	< 1.0	3
SO_4^{2-} (mg/L)	31	8	1	24	8	7	400	250
Na^+ (mg/L)	21.2	23.5	24.7	13.9	15.0	23.0	200	200
K^+ (mg/L)	1.6	2.2	1.8	1.6	1.4	1.3	12	–
Ca^{2+} (mg/L)	43.1	46.9	62.3	30.6	39.6	55.3	75	–
Mg^{2+} (mg/L)	11.4	13.2	17.0	8.8	14.6	14.9	30.0–35.0	–
NH_4^+ (mg/L)	0.1	0.1	0.2	0.1	0.1	0.1	0.5	1.5
PO_4^{3-} (mg/L)	0.3	0.2	0.2	0.4	0.2	0.3	6	0.01

strong negative correlation ($r < -0.7$) was observed between PO_4^{3-} and EC, hardness, and Cl^-, mainly due to the ability of PO_4^{3-} to precipitate when combined with cations, which ultimately reduces concentrations of ions in groundwater.

From the Piper diagram, all groundwater samples fell into the Mg–HCO_3 type or the mixed type, and alkaline earths exceeded alkali metals, indicating that the major ions were from natural geologic sources (Fig. 6). The study was conducted in late May, which is the early stage of the monsoon season. In this period, dissolution of minerals and substantial groundwater recharge occur via infiltration to groundwater.

WQI results range from 26.9 to 61.8 (Table 7). All groundwater sites, except GW-2, fall in the "excellent-water" category. GW-2 falls in the category of "good water", mainly because of the detection of Cr which exceeded DoE guidelines. Chromium contamination contributes to over half of the WQI of GW-2. Beyond these data, deep groundwater in the study area is, overall, in excellent condition. However, it should be kept in mind that WQI is an overall indication of water quality; specific concerns, in this case, Cr contamination, should be examined even when WQI is in "good" condition due to the positive values of most other contributors.

Combining physicochemical analysis with metal analysis, we conclude that while groundwater was generally in excellent condition, it has been contaminated in localized zones. Due to the increasing permeability with increasing depth in the aquifer (Halim et al. 2011), contamination is expected to spread relatively rapidly into groundwater. Urgent action is needed to protect drinking water sources and soil of Hazaribagh. A brief discussion for options of treatment appears in the next section.

Optional treatments

With the removal of tanneries from Hazaribagh, the government of Bangladesh is developing plans for its eventual use as a residential area within the framework of the Dhaka Detailed Area Plan (Bhowmik 2013). Given its potential utilization for residences and small businesses, it is essential that necessary steps be taken for mitigating pollution in the area. Remediation of surface soil and groundwater is essential prior to implementing any redevelopment plan. Provided below are three optional strategies for treatment of soil and groundwater of Hazaribagh (as also illustrated in Fig. 7).

Soil flushing is a widely used remediation method which can extract metallic pollutants (e.g., Cr, Zn, Cu)

Table 6 Correlation coefficient matrix between different physiochemical variables in groundwater at Hazaribagh tannery sites

	Depth (m)	EC	Alk	Hardness	TDS	Cl^-	NO_3-N	NO_2-N	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	PO_4^{3-}
Depth (m)	1														
EC	0.43	1													
Alk	0.26	0.33	1												
Hardness	0.67	**0.89**	0.48	1											
TDS	0.22	**0.90**	0.18	0.64	1										
Cl^-	0.19	**0.74**	− 0.38	0.51	0.72	1									
NO_3-N	− 0.68	− 0.04	0.13	− 0.16	− 0.10	0.01	1								
NO_2-N	− 0.14	0.00	**0.66**	0.25	− 0.28	− 0.41	0.54	1							
SO_4^{2-}	− 0.28	**− 0.85**	**− 0.74**	**− 0.79**	**− 0.76**	− 0.31	− 0.15	− 0.33	1						
Na^+	− 0.06	0.61	− 0.12	0.34	**0.83**	0.59	− 0.24	− 0.38	− 0.42	1					
K^+	− 0.46	0.25	− 0.34	− 0.19	0.51	0.55	0.40	− 0.49	− 0.14	0.41	1				
Ca^{2+}	0.34	**0.79**	0.26	0.66	**0.88**	0.48	− 0.42	− 0.21	− 0.68	**0.88**	0.12	1			
Mg^{2+}	0.56	**0.95**	0.47	**0.94**	**0.83**	0.55	− 0.23	0.09	**− 0.86**	0.61	− 0.01	**0.87**	1		
NH_4^+	0.62	0.59	0.22	0.46	**0.71**	0.36	− 0.60	− 0.55	− 0.51	0.48	0.23	0.69	0.62	1	
PO_4^{3-}	− 0.32	**− 0.94**	− 0.13	**− 0.81**	**− 0.79**	**− 0.86**	− 0.17	0.00	**0.70**	− 0.47	− 0.38	− 0.55	**− 0.79**	− 0.40	1

Bolded values have strong positive correlation (> 0.7) or negative correlation (< − 0.7)

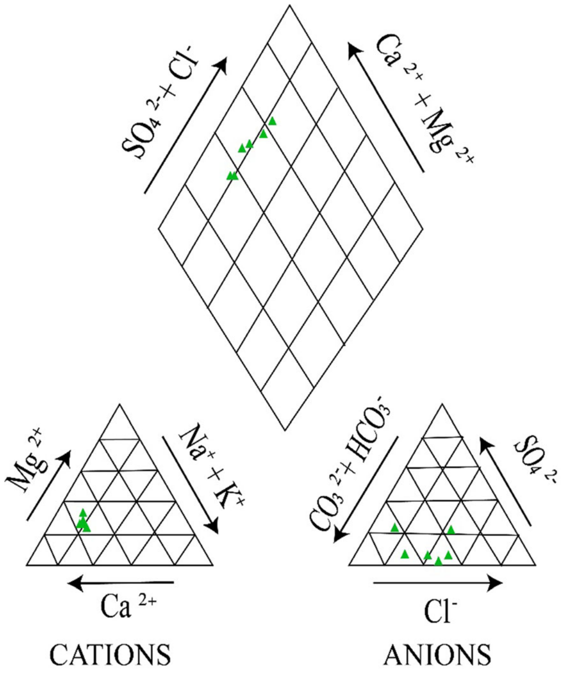

Fig. 6 Piper diagram illustrating physiochemical characteristics of groundwater

Table 7 Calculated Water Quality Index (WQI) for groundwater samples of six sites

Sample Site	WQI	Water type
GW-1	26.9	Excellent
GW-2	61.8	Good
GW-3	35.4	Excellent
GW-4	27.7	Excellent
GW-5	35.5	Excellent
GW-6	33.4	Excellent

and some organic contaminants (Lombi and Hamon 2005; Hashim et al. 2011). This technology is optimized when the contaminants can be readily mobilized and when soil hydraulic conductivity is medium to high. The Cr, Zn and Cu present at Hazaribagh may be solubilized with a dilute chelating agent, for example ethylenediaminetetra acetic acid (EDTA). The EDTA is most effectively used when it is injected directly into the affected metallic plume. Following extraction, the metals may be converted to less toxic and/or less mobile forms; for example, Cr(VI) is reduced to the less hazardous trivalent form and can potentially be recycled (Choppala et al. 2013). Reddy and Al-Hamdan (2013) measured total removal efficiencies of 76%, 63% and 11% for Pb, Zn and Cu, respectively, when flushing a soil with 0.2 M EDTA.

The upper part of the aquifer in the study area is composed primarily of fine sand and sand, with relatively high hydraulic conductivity. Our findings show spatially isolated patterns where specific regions are enriched in certain elements. This may simplify targeting the plume using soil flushing. For example, flushing could be applied to the NE side of the study area for removal of Cu, Zn, Ni and Cd, and applied to the SW for Pb, and SE for Cr. Potential contamination to groundwater is a concern when using soil flushing, however. It is essential that the direction of groundwater flow be determined accurately in order to capture newly solubilized metals. Considering that groundwater is the main drinking water source of the region, it is advised that soil flushing be applied only in spots where contamination is heaviest.

Electrokinetic remediation (ER) involves the use of direct electric current to remove metallic contaminants from soil by creation of a differential electrical potential. ER removes positively charged metals and also anions such as chromate via desorption and subsequent transport to a set of cathodes. Removal of Cr(VI) is relatively effective in ER, as this species is highly mobile in soil (Pichtel 2019). Chu et al. (2018) measured 57% and 69.9% removal of Pb and Cd in soil, respectively, with an electrokinetic system. ER has the advantage of minimal surface disturbance and is feasible in the Hazaribagh district due to the high Cr levels combined with relatively high hydraulic conductivity.

Phytoremediation involves the use of specially selected plants for treating contaminated soil. In so-called phytoextraction, metals are taken up by roots, translocated and accumulated to shoots (Rafati et al. 2011). However, transferring metals from roots to shoots is a difficult process for many species. Another application of phytoremediation is termed phytostabilization, where metals are adsorbed to roots and/or converted to a less mobile form. With phytostabilization, the mobility of metals is decreased; thus, their bioavailability is reduced, ultimately preventing leaching into groundwater (Rew 2007).

Phytoremediation is applicable for treatment of soils of the Hazaribagh district; however, this process requires more time as compared with soil flushing or

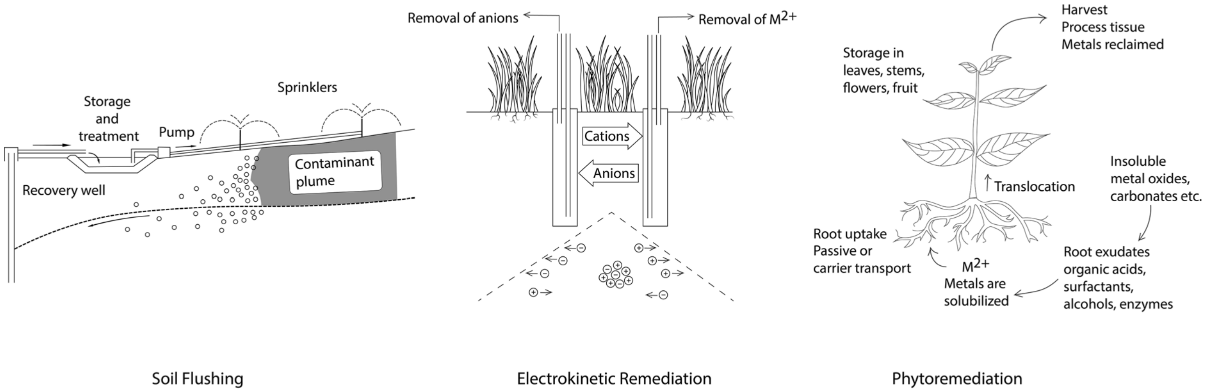

Fig. 7 Schematic illustration of three suggested metal remediation technologies for the study area

electrokinetics. Another limitation of phytoremediation is that it is successful only to the depth of the root zone. However, reducing metal contamination at shallow depths will ultimately reduce the risk of leaching to groundwater. Due to the fact that: (1) shallow soil was heavily contaminated in the study area; (2) phytoremediation poses no side effects to groundwater; and (3) the technology is cost-effective, phytoremediation is recommended for long-term treatment of surface contaminants in the study area.

Even with remediation, vegetable plantings should be prohibited at the site, and restrictions should be implemented on direct utilization of groundwater for drinking purposes without further treatment.

Conclusions

The soil of Dhaka's Hazaribagh district is contaminated by metals including Cr, Zn and Cu to various extent. Other metals did not appear elevated when compared to the accepted national and international standards. Due to the high concentration and mobility of Cr, deep groundwater is also contaminated by Cr at one location. Due to the low hydraulic gradient and high hydraulic conductivity of the local soil, concentrations of metals exhibit considerable spatial variation and are likely transported vertically in the soil profile.

Other than Cr contamination in one sampling site, deep groundwater is, overall, in excellent quality based on WQI. Physiochemical parameters of the groundwater samples as analyzed using a Piper diagram, correlation coefficient matrix, and a simple WQI indicate that groundwater is generally in excellent quality, with recharge from natural sources.

Three remediation techniques, including soil flushing, ER and phytoremediation, are suggested for remediating soil and thus reduce stress of groundwater contamination. It is recommended that soil flushing and ER be conducted as a short-term solution, while phytotreatment serves as a long-term remediation technology. The latter treatment can take place concurrently with operation of public parks and recreational areas.

Data collected in this study are confined to limited points at sample collection time. Soil texture/composition tests would be an asset in interpreting metal mobility and groundwater movement. An additional long-term environmental monitoring program is suggested to establish a record of changes in environmental conditions and to monitor the effectiveness of remediation practices. Follow-up studies that include additional analyses of surface water, groundwater and soil are needed. It is also suggested that even after remediation processes have ceased, natural recovery like vegetation planting should be conducted in Hazaribagh to continuously remove pollutants which may re-accumulate from surrounding areas or aquifers. Ensuring the natural recovery of soil and groundwater is critical for sustainable development of the region as both a business and residential area.

Acknowledgements This work was made possible by the Ball State New Faculty Startup under fund number 120198, and the Ball State ASPiRE Graduate Student Research Support under award number A19-0319. This research was also supported by Professor Dr. Md. Delwar Hossain of Department of Civil Engineering, Bangladesh University of Engineering and

Technology. The authors also want to thank two anonymous reviewers for their help in improving the manuscript.

References

Aggarwal, A., Hoppe, M., & Walkenhorst, P. (2009). Special economic zones and economic diversification: Some evidence from South Asia. In R. Newfarmer, W. Shaw, & P. Walkenhorst (Eds.), *Breaking into new markets* (pp. 223–236). Washington, DC: World Bank.

Ahmad, M. K., Islam, S., Rahman, M. S., Haque, M. R., & Islam, M. M. (2010). Metals in water, sediment and some fishes of Buriganga River, Bangladesh. *International Journal of Environmental Research, 4*(2), 321–332.

Alvarez-Bernal, D., Contreras-Ramos, S. M., Trujillo-Tapia, N., Olalde-Portugal, V., Frías-Hernández, J. T., & Dendooven, L. (2006). Effects of tanneries wastewater on chemical and biological soil characteristics. *Applied Soil Ecology, 33*(3), 269–277.

Aravindhan, R., Madhan, B., Rao, J. R., Nair, B. U., & Ramasami, T. (2004). Bioaccumulation of chromium from tannery wastewater: An approach for chrome recovery and reuse. *Environmental Science and Technology, 38*(1), 300–306.

Arias-Barreiro, C. R., Nishizaki, H., Okubo, K., Aoyama, I., & Mori, I. C. (2010). Ecotoxicological characterization of tannery wastewater in Dhaka, Bangladesh. *Journal of environmental biology, 31*(4), 471–475.

ASTM D4972-13. (2013). *Standard test method for pH of soils*. West Conshohocken, PA: ASTM International. www.astm.org. Last Retrieved 10-08-2019.

Bangladesh Meteorological Department. (2019). http://bmd.gov.bd/. Last Retrieved 10-08-2019.

Batabyal, A. K., & Chakraborty, S. (2015). Hydrogeochemistry and water quality index in the assessment of groundwater quality for drinking uses. *Water Environment Research, 87*(7), 607–617.

Bhowmik, A. K. (2013). Industries' location as jeopardy for sustainable urban development in Asia: A review of the Bangladesh leather processing industry relocation plan. *Environment and Urbanization Asia, 4*(1), 93–119.

Chadha, D. K. (1999). A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeology Journal, 7*(5), 431–439.

Choppala, G., Bolan, N., & Park, J. H. (2013). Chromium contamination and its risk management in complex environmental settings. In *Advances in agronomy* (Vol. 120, pp. 129–172). Cambridge: Academic Press. https://doi.org/10.1016/b978-0-12-407686-0.00002-6.

Chu, G., Xiao, J., Zhang, Y., Dong, P., Nayaka, G. P., Meng, Q., et al. (2018). Multi-electrode system for electrokinetic remediation of paddy soil to remove toxic metals. *International Journal of Electrochemical Science, 13,* 11335–11346.

Cude, C. G. (2001). Oregon water quality index a tool for evaluating water quality management effectiveness 1. *JAWRA Journal of the American Water Resources Association, 37*(1), 125–137.

Dong, D., Zhao, X., Hua, X., Liu, J., & Gao, M. (2009). Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China. *Journal of Hazardous Materials, 162*(2–3), 1261–1268.

FAO. (1988). *Land resources appraisal of Bangladesh for agricultural development* (Vol. 2). Rome: FAO.

Gebrekidan, A., Weldegebriel, Y., Hadera, A., & Van der Bruggen, B. (2013). Toxicological assessment of metals accumulated in vegetables and fruits grown in Ginfel River near Sheba Tannery, Tigray, Northern Ethiopia. *Ecotoxicology and Environmental Safety, 95,* 171–178.

Halim, M. A., Sumayed, S. M., Majumder, R. K., Ahmed, N., Rabbani, A., & Karmaker, S. (2011). Study on groundwater, river water and tannery effluent quality in Southwestern Dhaka, Bangladesh: Insights from multivariate statistical analysis. *Journal of Natural Science and Sustainable Technology, 5*(3), 125–147.

Harkins, R. D. (1974). An objective water quality index. *Journal of Water Pollution Control Federation, 46,* 588–591.

Hashem, M. A., Tomal, M. N. A., & Mondal, B. K. (2015). Generation of fleshings at beamhouse in tannery and its environmental impact assessment: Bangladesh perspective. *Bangladesh Journal of Scientific and Industrial Research, 50*(3), 227–232.

Hashim, M. A., Mukhopadhyay, S., Sahu, J. N., & Sengupta, B. (2011). Remediation technologies for metal contaminated groundwater. *Journal of Environmental Management, 92*(10), 2355–2388.

Horton, R. K. (1965). An index number system for rating water quality. *Journal of Water Pollution Control Federation, 37*(3), 300–306.

Hossain, S. (2008). Rapid urban growth and poverty in Dhaka City. *Bangladesh e-Journal of Sociology, 5*(1), 57–80.

Huq, S. I. (1998). Critical environmental issues relating to tanning industries in Bangladesh. In R. Naidu, I. R. Willet, S. Mahimairaja, R. Kookana, & K. Ramasamy (Eds.), *ACIAR proceedings* (pp. 22–28). Coimbatore: ACIAR.

Islam, M., Karim, M., Zheng, X., & Li, X. (2018). Metal and metalloid pollution of soil, water and foods in Bangladesh: A critical review. *International Journal of Environmental Research and Public Health, 15*(12), 2825.

Jacobs, J. A., & Testa, S. M. (2005). *Overview of chromium(VI) in the environment: Background and history. Chromium(VI) handbook* (pp. 1–21). New York: CRC Press.

Juel, M. A. I., Chowdhury, Z. U. M., Mizan, A., & Alam, M. S. (2016). Toxicity and environmental impact assessment of metals contaminated soil of Hazaribagh Tannery Area. In *International conference on advances in civil engineering* (pp. 21–23).

Karn, S. K., & Harada, H. (2001). Surface water pollution in three urban territories of Nepal, India, and Bangladesh. *Environmental Management, 28*(4), 483–496.

Lombi, E., & Hamon, R. E. (2005). Remediation of polluted soils. In D. Hillel (Ed.), *Encyclopedia of soils in the environment* (pp. 379–385). Amsterdam: Elsevier. https://doi.org/10.1016/b0-12-348530-4/00087-4.

Maier, J., Kandelbauer, A., Erlacher, A., Cavaco-Paulo, A., & Gubits, G. M. (2004). A new alkali-thermostable azoreductase from *Bacillus* sp. strain SF. *Applied Environmental*

Microbiology, 70, 837–844. https://doi.org/10.1128/AEM.70.2.837-844.2004.

Mondol, M., Asia, A., Chamon, A., & Faiz, S. (2017). Contamination of soil and plant by the Hazribagh tannery industries. *Journal of the Asiatic Society of Bangladesh, Science, 43*(2), 207–222.

Namaghi, H. H., Karami, G. H., & Saadat, S. (2011). A study on chemical properties of groundwater and soil in ophiolitic rocks in Firuzabad, east of Shahrood, Iran: With emphasis to metal contamination. *Environmental Monitoring and Assessment, 174*(1–4), 573–583.

Pichtel, J. (2019). *Fundamentals of site remediation: For metal- and hydrocarbon-contaminated soils* (3rd ed.). Rockville, MD: Government Institutes.

Rafati, M., Khorasani, N., Moattar, F., Shirvany, A., Moraghebi, F., & Hosseinzadeh, S. (2011). Phytoremediation potential of *Populus alba* and *Morus alba* for cadmium, chromium and nickel absorption from polluted soil. *International Journal of Environmental Research, 5*(4), 961–970.

Rayment, G. E., & Higginson, F. R. (1992). *Australian laboratory handbook of soil and water chemical methods*. Port Melbourne: Reed International Books Australia P/L, Trading as Inkata Press.

Reddy, K. R., & Al-Hamdan, A. Z. (2013). Enhanced sequential flushing process for removal of mixed contaminants from soils. *Water, Air, and Soil Pollution, 224*(12), 1709.

Rew, A. (2007). Phytoremediation: An environmentally sound technology for pollution prevention, control and remediation in developing countries. *Educational Research and Reviews, 2*(7), 151–156.

Shakir, L., Ejaz, S., Ashraf, M., Qureshi, N. A., Anjum, A. A., Iltaf, I., et al. (2012). Ecotoxicological risks associated with tannery effluent wastewater. *Environmental Toxicology and Pharmacology, 34*(2), 180–191.

Sherene, T. (2010). Mobility and transport of metals in polluted soil environment. *Biological Forum: An International Journal, 2*(2), 112–121.

Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., & Sutton, D. J. (2012). Metal toxicity and the environment. In A. Luch (Ed.), *Molecular, clinical and environmental toxicology* (pp. 133–164). Basel: Springer.

Tyagi, S., Sharma, B., Singh, P., & Dobhal, R. (2013). Water quality assessment in terms of water quality index. *American Journal of Water Resources, 1*(3), 34–38.

Wuana, R. A., & Okieimen, F. E. (2011). Metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *Isrn Ecology*, *2011*, 1–20.

Zahid, A., Balke, K. D., Hassan, M. Q., & Flegr, M. (2006). Evaluation of aquifer environment under Hazaribagh leather processing zone of Dhaka city. *Environmental Geology, 50*(4), 495–504.