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Hydrogeochemical Study and Geospatial Analysis of Water Quality Using GIS based Water Index and Multivariate Statistics in Kombolcha City, Ethiopia

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Abstract

The study was carried out to evaluate hydro geochemistry and the risk of groundwater and surface water pollution in the Kombolcha area. To achieve this, hydrogeochemical analysis, water heavy metal, geospatial data analysis, ion ratio, correlation matrix, principal component analysis, Heavy metal Pollution Index (HPI), and Water Quality Index (WQI) methodologies were employed. A total of 36 samples (both water and effluent samples) had been collected and assessed for major physicochemical variables and heavy metals and samples were taken from hand dug wells, Borehole, springs, and rivers in the area. Hydrogeochemical methods showed groundwater mineralization due to (1) silicate weathering, (2) cation exchange processes, and (3) anthropogenic sources (i.e., contaminated discharge of sulphate, carbonate, and trace metal effluents). The study result revealed that major ions dominating the area are Ca^{2+} >Na^{+} > Mg^{2+} >K^{+}, HCO_{3}^{-} >SO_{4}^{2-} > Cl- > NO3-, and Fe> Mn >Pb> Cr> Cd for cations, anions and trace metals respectively with all heavy netals had mean concentrations above the WHO recommended limits. Calculated Pollution indices revealed 50.7% of the sample belongs to a low level of pollution, while 35% and 14.3% belong to a medium and high level of pollution respectively which consequently translating the area into high groundwater pollution zones. The correlation matrix revealed that no significant correlation exists between the water quality variables (Cl and NO3- with Fe, Pb, Cr, Mn, and Cd). PCA was applied on the data set to identify the spatial sources of pollution in groundwater and in the first principal component analysis, Mn, Fe, Cr, Pb, and Cd (in descending order) were found in amounts greater than 0.5, confirming that these metals were from anthropogenic sources. The combined assessments based on WQI and HPI, the study showed that water samples in the proximity of industrial sites are polluted by factories effluent and uncontrolled waste disposal due to urbanization.

Keywords: Groundwater Quality, Heavy Metal Pollution Indices, Correlation Matrix, Heavy Metal Pollution Index, PCA.

1. Introduction

Natural resources are continuously degraded due to populace blast, global climate change, poor management, and misconception of the nature of assets which is resulted from lack of coordination and coordinated approaches [1, 2]. As of late, due to impromptu development of industrialization and quick urbanization, groundwater quality has become a major concern in the world [3, 4]. Urban zones produce both nonpoint and point sources of contaminants, and alongside these industrial effluents, poisonous metals are discharged, as a result the health of rivers worldwide has been impacted by the nation's economy's and population's rapid industrialization. Most rivers that flow through cities are polluted by municipal waste and industrial effluents [5, 6]. The contamination of water due to heavy metals (HMs) is a big concern for humankind; however, global studies related to this topic are rare [7]. Under certain environmental conditions, defilement of water by heavy metals (HMs) could accumulate to a toxic concentration level and cause significant ecological impacts and serious health issue [8, 9]. Many hydrogeochemical studies have shown that heavy metal toxicity leads to cardiovascular, neurological, and renal problems [10]. The main health hazards caused by chemical pollution of water are due to the presence of nitrates, chromium, cadmium, manganese, zinc, lead, and other toxic substances [11, 8] Physicochemical water quality checking is basic to characterize the quality of surface water, and groundwater with time and space. It too makes a difference to recognize the source of contamination [12, 13]. Evaluation of groundwater quality is exceptionally complex that undertaking various parameters capable of causing stresses on groundwater quality [14-16]. However, characterization of groundwater quality in Kombolcha by using integrated appropriate methodologies is not carried out yet. Therefore, this study has been aimed to justify an integrated approach that includes heavy metal pollution indices and multivariate statistics

to characterize the groundwater quality in the Kombolcha district of north eastern Ethiopia. Heavy metal pollution index (HPI), is used to evaluate the hazardous metal pollution in drinking water purposes [17]. A few measurable strategies (Several statistical methods) have been utilized for the evaluation of groundwater quality within the world. For example, multivariate statistical methods offer to identify conceivable factors/sources that impact water frameworks and provides as a tool for reliable water resources management as well as quick solution to pollution problems in many part of the world including Kombolcha.

1.1. Geology and Hydrogeology

Ethiopia is covered by Basement complex, Paleozoic, and Mesozoic sedimentary rock, and Cenozoic volcanism and sediments Geological Survey of Ethiopia [18]. The Kombolcha area occupies the southwestern block of the Afar Depression and the southwestern Afar Depression merges southward with the northeast striking of Main Ethiopian Rift (MER), and eastward with the east striking of Gulf of Aden [19]. The geological history of the studied area is related to the evolution and development of the Ethiopian Plateau and the Rift system and it is dominated by volcanic rocks of the Eocene to Oligocene to recent or quaternary sediments [20].

The major lithologic units found in the study area include Basalt, Rhyolitic Ignimbrite, and Alluvial deposits and, the lithologic units are classified into three hydrogeologic groups as very low, Low, and moderately productive group based on transmissivity which ranges from 1.72-59.8 (m2/d).

2. Materials and Methods

2.1. Study area

It is found within the western edge of the Main Ethiopian Rift valley (MER) and canter of Borkena River catchment, within projected coordinate system UTM, 37p, 1218460 to 1233940mN, and 571354 to 582900mE, and it covers an area of 136.98 km2. Groundwater is the main source of drinking water in Kombolcha. Subsequently, neighborhood individuals in the study area are fully depended on this groundwater for their daily life.

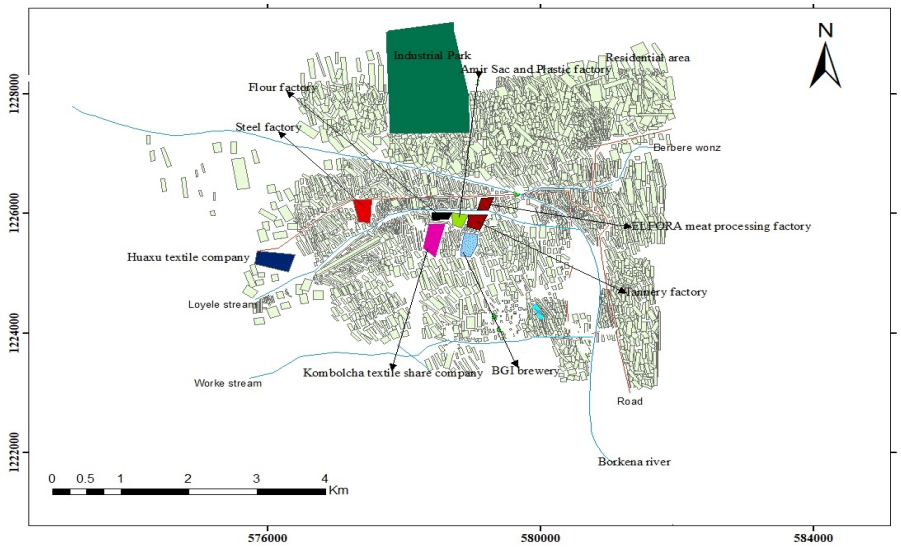

Figure 1: The location of the study area within the industrializing Kombolcha city administration including main rivers the Borkena River and factories discharging effluents into its tributaries

2.2. Sample Collection and Analytical Procedure

To evaluate the quality and pollution status, representative water samples were collected systematically. Samples were taken where industrial effluents were directly mixed with streams/rivers, from nearby wells, and where more municipal wastes were discharged. The sampling device (plastic bottles) were cleaned very well before use for sampling to prevent mixing up of water and contamination if something remains in the bottle before sampling. A total number of 36 samples were collected in February, 2021 from groundwater and surface water sources (hand-dug wells, deep wells, springs, and rivers) across the industrial area in preselected sampling points. The geographical location of each sampling point was determined with a handheld global positioning system (GPS). For further chemical analysis, the samples were sealed tightly and were taken to the laboratory.

During the fieldwork, different water quality data were collected from different water resources such as boreholes, hand-dug wells, springs, and rivers. The data include pH, temperature, EC, and TDS using HANNA HI9813-6 portable multiparametric probe, which was calibrated appropriately before being used each day using calibration solution. The probe was first calibrated with pH 7.0 and then by pH 10 calibration solution.

After representative water samples collected from boreholes, springs, hand-dug wells, and rivers in the area, it were sealed tightly and taken to the laboratory for the analysis of major ions like Ca^{2+} >Na^{+} > Mg^{2+} >K^{+}, HCO_{3-} >$SO4^{2-}$ > Cl^{-} > NO_{3}-, and heavy metals such as chromium (Cr), cadmium (Cd), iron (Fe), manganese (Mn), and lead (Pb). Calcium (Ca2+), magnesium (Mg2+) Sodium (Na+) and Potassium (K+) were analyzed using a flame photometer. Trace metal analyses were done at Addis

Ababa University using ZEEnit 700 P (Analytikjena) flame atomic absorption spectrophotometry (FAAS). Also, Sulfate (SO_4-) and bicarbonate (HCO_3-) analyzed by spectrophotometer. The FAAS detection limit varies for different trace metals. For heavy metal concentration analysis, 50ml samples of water were digested with 1ml (60-70%) of concentrated nitric acid (HNO3) and 0.5ml (36-40%) concentrated hydrochloric acid (HCl).

The anions of Nitrate (NO_3-) and chloride (Cl-) the samples were identified using ELE international paqualab photometer in Amhara Design and Supervision Enterprise Work (ADSWE) after Nitriphot No1 and Nitriphot No 2 tablets were added with10 ml of water samples. Moreover, pH, EC, TDS, and temperature were measured during the sampling. The water chemistry data were used to determine the water quality/pollution in the study area, and to correlate the water chemistry variation with geology, agricultural inputs, industrial, or other anthropogenic sources. In this case, the most important thing was to achieve the quality control /quality assurance of the laboratory analysis technique, which was by checking the sample container and regents, using blank samples, and run samples in triplicate and the mean values have been taken.

In the use of FAAS for heavy metal analysis optimization of the operating conditions of the instrument is very crucial. Therefore, the analysis of Cd, Cr, Fe, Mn, and Pb began with selection and adjustments of various units of the FAAS (i.e., lamp selection, wavelength selection, slit adjustment, energy, flame adjustment, and detection limit) as shown in Table 1.

Parameter	**Unit**	**Cd**	**Pb**	**Cr**	**Fe**	**Mn**
Wavelength	**nm**	**228.8**	**383.3**	**357.9**	**248.3**	**279.5**
Energy	Nm	70.4	69.7	69.1	69.7	73.2
Lamp current	mA	2	2	4	4	5
Slit width	nm	1.2	1.2	0.2	0.2	0.2
PMT	…….	301	382	275	376	348
Detection limit	**mg/l**	**0.002**	**0.06**	**0.01**	**…….**	**……**

Table 1: Instrumental operating conditions for determination of heavy metals in ground and surface water samples using Flame AAS

3.3. Water quality index (WQI)

There are several water quality assessment methods available, and these methods are dependent on the physicochemical parameters which are used in various ways to assess the quality of groundwater for drinking purposes (Chegbeleh et al., 2020). Many studies have adopted the Water Quality Index (WQI) method, and successfully assessed the suitability of water for drinking purposes (Oboh, 2017). The study adopted the weighted arithmetic index approach (Brown et al., 1972), in conjunction with Piper diagrams in characterizing the chemistry of groundwater in the study area. The WHO (2017) guidelines for drinking water were used for the computation of WQI. According to Ramakrishnaiah et al. (2009), computation of the WQI to assess the suitability of groundwater for drinking purposes is a four-step approach:

Step 1: each of the 15 parameters has been assigned a weight (wi) according to its relative importance in the overall quality of water for drinking purposes and pollution (see Table 6.3). The maximum weight of 5 has been assigned to parameters like total dissolved solids (TDS) and nitrate (NO3), chromium (Cr), cadmium (Cd), lead (Pb), iron (Fe), and manganese (Mn) due to their major importance in water quality assessment in the study area due to industrialization and urbanization. The remaining other parameters were assigned a weight between 1 and 5 depending on their importance in the overall quality of water for drinking purposes (Zakhem and Hafez, 2018; Bawoke & Anteneh, 2020; Chegelebah et al., 2020).
Step 2: involves the computation of the relative weight (Wi) of each parameter using:

$$Wi = \frac{wi}{\sum_{i=1}^{n} wi} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (5)$$

Where, Wi is the relative weight, wi is the weight of each parameter and n is the number of parameters
Step 3: computation of the quality rating scale (qi) for each parameter

$$qi = \frac{Ci}{S} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots (6)$$

Where, qi, is the quality rating, Ci is the monitored concentration of each parameter in mg/l, and S is the (WHO , 2017) standard for each parameter in mg/l.

Step 4: determination of the sub-index (SI) for each parameter is used to calculate the WQI

$$SI = Wi \times qi \dots\dots\dots\dots\dots\dots\dots (7)$$

Then, the overall WQI was computed by summing up all the sub-index values for each sample as follow

$$WQI = \sum_{I=1}^{n} SI \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (8)$$

Using the above procedure, the WQI of the sampled water was made (Brown et al., 1972) and it was compared with standards. Table 6 3: WHO standards, weight (wi) for each parameter of the groundwater and surface water samples in the area (WHO, 2017)

Unit is in (mg/l) except pH (unit less)	(WHO, 2017), standards	Weight (wi)
pH	**6.5-8.5**	**4**
TDS	500	5
HCO_3–	150	3
Na^+	200	3
Ca^{2+}	200	3
Mg^{2+}	150	3
K^+	3000	2
Cl^-	250	4
$SO4^{2-}$	250	4
NO_3^-	50	5
Fe	0.3	5
Cd	0.003	5
Cr	0.005	5
Pb	0.01	5
Mn	0.1	5
		∑ wi=61

Table 6 1: WHO standards, weight (wi) for each parameter of the groundwater and surface water samples in the area (WHO, 2017)

WQI Ranges	Type of water
0-25	**Excellent water quality**
26–50	Good water quality
51–75	Poor water quality
76–100	Very poor water quality
Above 100	Unfit /unsuitable for drinking

Table 6.2: Classification of computed WQI values for human consumption after (Brown et al., 1972).

3.4 Heavy Metal Pollution Index (HPI)

Heavy metal pollution index (HPI) is a rating method and an effective tool to assess the water quality for heavy metals (Zakhem and Hafez, 2018). HPI is calculated from the point of view of the suitability of ground water for human consumption with respect to metals contamination (Moldovan et al., 2022) using the standards (Table 3) and classified based on(Table 2) . and it is important for assigning a weightage (Wi) for each selected parameter, and it is computed using the following equation (Islam et al., 2016).

$$HPI = \frac{\sum_{i=1}^{n} WiQi}{\sum_{i=1}^{n} Wi} \dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Where, Wi is the relative weight or weighting factor for each chosen parameter defined as equation (2) below; Qi is the sub-index /individual quality rating /for the ith heavy metal ion calculated for each parameter using Equation (3) and n is the number of parameters.

$$Wi = \frac{wi}{\sum_{i=1}^{n} wi} \dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

The sub-index, Qi, is computed by:

$$Qi = \sum_{i=1}^{n} \frac{(Mi - Ii)}{(Si - Ii)} \times 100 \dots\dots\dots\dots\dots\dots\dots (3)$$

Where, wi means the unit weight factor for the ith heavy metal, which is inversely proportional to the standard value S of the corresponding parameter as defined in Equation (4).

Mi: is the measured concentration value of each parameter in the groundwater and surface water samples; Ii and Si indicate the highest desirable that was taken in according to World Health Organization (WHO, 2017) and maximum permissible value (taken as 1, 0.3, 0.05, 0.01,and 0.05mg/l for Fe, Mn, Pb, Cd, and Cr from Bureau of Indian Standards (BIS, 2003) of the i^{th} parameters respectively for this study.

$$wi \propto \frac{1}{S} = \frac{k}{S} = \frac{1}{S} \dots\dots\dots\dots\dots\dots\dots\dots (4)$$

Where, S is the standard value, and the proportionality factor k is taken equal to one for all metals in the study (Eldaw et al., 2020).

Category	Degree of pollution/Water class
<45	Low
45-90	Medium
>90	High

Table 2: Classification of the ground water quality based on categories of quality indices values after(Islam et al., 2016)

Parameter	Standard, S (mg/l)	Weight (wi) (1/S)	Relative weight (Wi)
Fe	0.3	3.3	0.0053
Mn	0.1	10	0.0159
Cd	0.003	333.3	0.5319
Cr	0.005	200	0.31917
Pb	0.01	100	0.15958
			Σwi = 646.6

Table 3: WHO standards, weight (w), calculated relative weight for each parameters of the groundwater and surface water samples in the area (World Health Organization, 2017)

3.5. Principal Component Analysis

In this study, the IBM SPSS v.26 software was used to analyze the dimensional groundwater quality data of the samples including Cl-, NO3-, Fe, Mn, Cr, Pb, and Cd. PCA is a quantification of the significance of variables that explain the observed grouping and patterns of the inherit properties of the individual (Nosrati et al., 2012; Dwivedi &Vankar, 2014). According to Dwivedi &Vankar, (2014), strong, moderate, and weak factor loadings range from >0.75, 0.75 to 0.5, and 0.5 to 0.3, respectively. PCA allow for explaining of related parameters by only one factor (Usman et al., 2014; Egbueri& Onitsha, 2020). It is an important factor responsible for variation in river and groundwater quality and eventually leads to sources identification of water pollution. The general procedure for groundwater quality characterization used in the study is shown in the flow chart below (Figure 2).

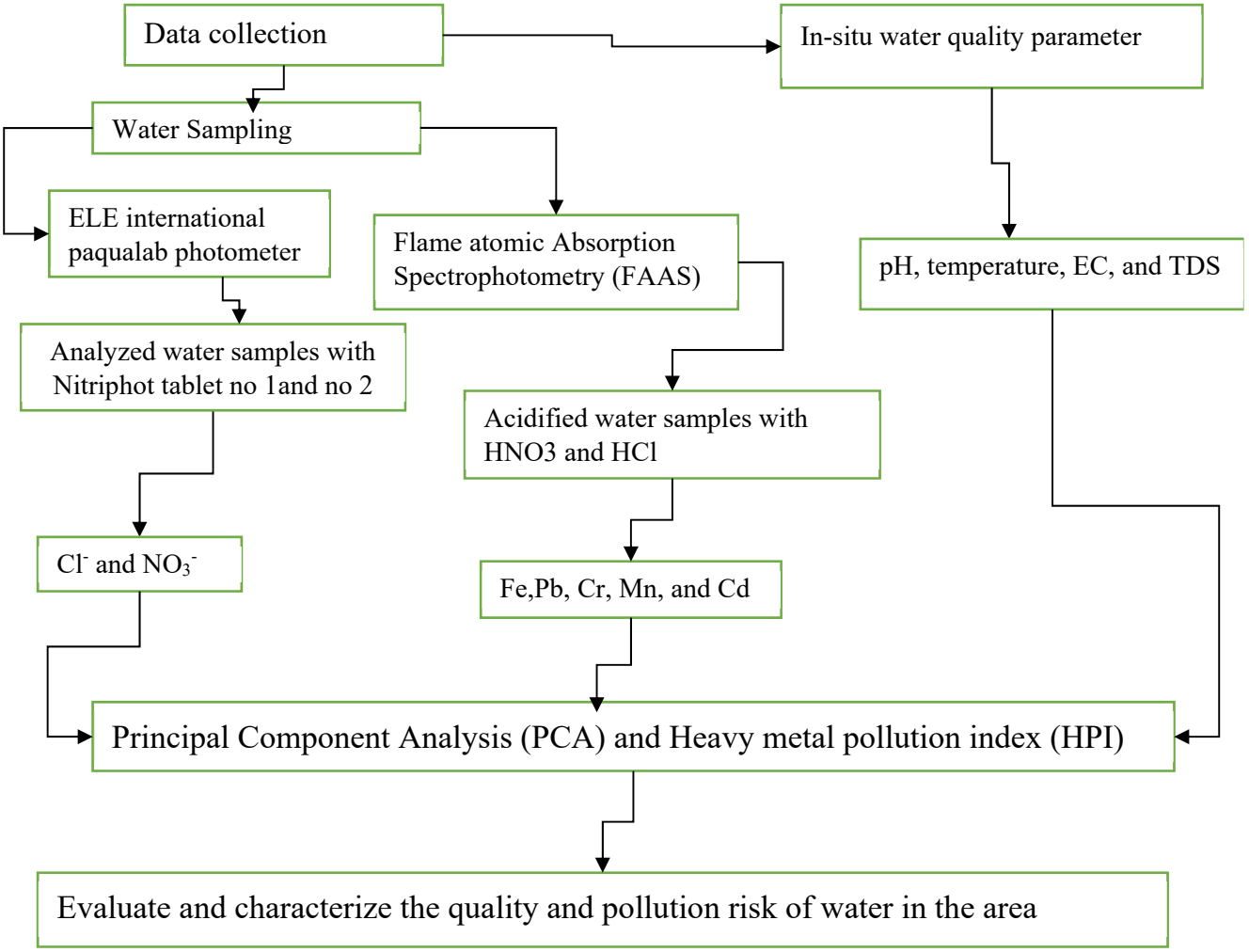

Figure 2: Flow chart showing the overall methodological approach applied in the study area

4. Results and Discussion

4.1. Physicochemical analysis

The result of the physicochemical analysis is presented in (Table 4) and the descriptive statistics in (Table 5).

Cadmium (Cd) variations are explained as the minimum, maximum, and mean values of 0.002, 0.36, and 0.045mg/l, respectively. The mean value of Cd is above the permissible limit of the (WHO, 2017) standard which is 0.003 mg/l.

The variation of manganese (Mn) and iron (Fe) is explained with the mean value of 0.259, and 0.422 mg/l respectively. The mean value of both Fe and Mn variables are above (WHO, 2017) standard limits which are 0.1 and 0.3 mg/l respectively. The groundwater with a higher value of Mn and Fe in spatial variation is closely related to the Steel and Huaxu textile factories the location of industries in (Figure1).

The minimum, maximum, and mean values of lead (Pb) and chromium (Cr), are 0.06, 1.071, and 0.146 for lead and 0.01, 1.032 and 0. 099mg/l for chromium. The mean value of both Pb and Cr are above (WHO, 2017)standard limits which are 0.01 and 0.005 mg/l respectively.

Station Id	Tem	pH	TDS	EC	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}	CO_3^{2-}	NO_3^{-}
BGI_1	29.2	8.04	341.65	523	55	5	0.73	31	24.07	69.63	1.2	18.6	16.48
BGI_3	29	8.27	351	551	29	4	0.29	21	22.85	63.9	45.6	1.7	11.38
BGI_4	28.1	8.32	458	680	26	4	0.52	38	21.11	81.7	55.8	1.6	10.57
ELF_W1	27.2	7.51	657.8	921	155	5.1	1.07	66.3	38.7	171.9	414	0.6	13.28
Tex_W1	28.1	7.6	448.5	629	85	4	0.91	41	31.5	82.7	201.2	0.7	13.2
Tex_W2	27	7.78	360.8	506	42	5	0.91	30	25.2	31.2	136.8	0.08	11.53
Tex_W3	28	8.3	333.9	328	36	4	0.62	32	21.7	52.4	81.6	0.8	15.2
Tex_W4	35.4	8.3	370.3	379	36	4	0.68	31	25.2	32.6	107.8	1.5	12.7
Tan_w	30.5	8.42	759.5	1065	148	10	11.09	44	26.2	155	364.9	1.6	10.68
KCTW_2R	27.5	8	343.7	482	76	6	0.69	25	19.87	72.3	159.6	1.5	12.93
SW_1	26.6	7.46	430	603	34	7	14.6	32	24.5	133.8	152.8	0.5	18.58
SW_2	28.4	8.06	353.9	503	32	6	8	31	23.53	88.9	185.19	1.3	22.9
BR_3	23.9	8.4	520	652	73	8	0.92	32	24.6	102.8	198.3	3.3	34.32
BBH-s	23.3	7.3	274	430	30	12.5	2.3	22	14	1.8	295	1.5	9.2
KMIW	26.7	7.1	194	320	103.8	6.5	4.6	46.7	6.6	14	224.5	3.4	3.54
BH	22.2	7.2	280	435	67	10	4	24	8.28	9.46	366	2.7	8.2
UBBH	20.4	6.9	204.31	327	136	13.2	3.3	6.6	10.5	2	230	1.9	7.9

	Tem	pH	TDS	EC	Cl-	NO_3^{-}	Fe	Cr	Cd	Pb	Mn
AHDW	24.8	7.6	392	469	24.1	18.9	0.01159	<0.01	<0.002	<0.06	0.01696
BOSP	26.8	7.7	485	680	27.5	19.6	0.021	<0.01	<0.002	<0.06	0.04158
BUHD	20.5	7.6	403	480	27.5	21.9	0.0096	<0.01	<0.002	<0.06	0.00592
HDBW	21.4	7.7	396	470	16.1	23.9	0.04828	<0.01	<0.002	<0.06	0.06192
HD1	23.1	7.5	613	760	14.5	19.2	0.96	<0.01	0.077	<0.06	0.06371
MHDW	23.6	7.9	382	440	21.5	18.9	0.06866	<0.01	<0.002	<0.06	0.06388
TA1	22.1	8.1	514	730	26.5	18.2	1.0639	1.032	<0.002	1.071	0.7209
UBSP	20.6	7.2	257	350	458	6.4	0.00754	<0.01	<0.002	<0.06	0.00828
BBH-p	27.3	8.1	289	384	22	20.2	0.05032	<0.01	<0.002	<0.06	0.3652
BGI W	22.7	8	414	530	22.3	15.3	0.336	0.04	0.07	0.08	0.3329
BGI S	25.5	8	466	580	18.4	14.7	0.9039	0.03	0.034	<0.06	0.4908
SB	24.6	7.8	482	533	11.8	7.6	1.586	<0.01	0.36	<0.06	0.9421
LSWJ	30.8	8.7	1370	1867	22.5	1.44	16.53	0.67	0.96	2.073	0.8427
BR1	25.8	8.4	656	870	31.9	36	1.136	0.073	0.47	0.0674	0.4628

Table 1: Physicochemical parameters of water samples

Parameter	Unit	Minimum	Maximum	Average	St. Dev.
Temperature	°C	20.4	35.4	27.38	3.32
pH	….	6.9	8.42	7.51	7.4
EC	µS/cm	320	1065	549.06	202.71
TDS	mg/l	194	759.5	393.02	146.8
Ca^{2+}	mg/l	26	155	74.11	41.54
Mg^{2+}	mg/l	4	13.2	6.82	2.76
Na^{+}	mg/l	6.6	66.3	32.56	12.83
K^{+}	mg/l	0.29	14.6	2.36	3.83
Cl^{-}	mg/l	6.6	38.7	21.67	8.11
NO_3-	mg/l	3.54	34.32	13.68	6.9
HCO_3-	mg/l	1.2	414	189.43	118.3
SO_4^{2}-	mg/l	1.8	171.9	68.59	51.67
Mn	mg/l	0.00592	0.9421	0.25951	0.31598
Fe	mg/l	0.00754	1.586	0.42223	0.55348
Cr	mg/l	0.01	1.032	0.0995	0.29446
Cd	mg/l	0.002	0.36	0.04475	0.09704
Pb	mg/l	0.06	1.071	0.14592	0.29138

Table 5: Descriptive statistics of the water samples in Kombolcha area

Even though, trace metals are found in the earth's crust, contamination in groundwater could be an outcome of natural and/or anthropogenic sources (Rani & Babu, 2008;Brindha et al., 2020). The aquifer type, the intensity of weathering of minerals from the aquifers, precipitation frequency, quality of the infiltrating water and residence time are the natural factors that control the presence of trace metals in groundwater (Aremu et al., 2010; Brindha et al., 2020). Anthropogenic sources are due to wastes from various industrial activities (e.g., tanning, electroplating, chemicals, and textile manufacturing) (Reyes-toscano et al., 2020). Commonly, trace amounts of metals usually found in freshwater are from the weathering of rocks and soils, and this may not exceed the international standard limit, and also may not deviate from the general trend in the area. However, significant concentration in water can usually be traced to mining, industrial, urban or agricultural sources (Rahman et al., 2020).

From (Table 6), the correlation matrix revealed that no significant correlation exists between the water quality variables (Cl- and NO_3- with Fe, Pb, Cr, Mn, and Cd). This indicates variation in the possible sources of the elements in the groundwater. Based on the geology of the study area, the results indicate that the presence of these parameters could not be majorly linked to geogenic origins, but more of anthropogenic origins as there are no geologic or ore deposits, that are rich in these heavy metals. pH has a strong correlation with Cd, Fe, and Pb. A high percentage of TDS and EC are supplied by Cd and Fe with R =0.939, and 0.835 respectively.

	pH	TDS	EC	NO_3-	Cl^{-}	Pb	Cd	Cr	Mn	Fe
pH	1	-0.651*	-0.697*	-0.299	-1.80E+01	**0.868****	**0.885**	0.378	-0.226	**0.727**
TDS		1	**0.981****	4.00E-02	0.356	**0.776**	**0.939****	-0.216	0.266	**0.835**
EC			1	6.90E-02	0.389	**0.857**	**0.946****	-0.163	0.313	**0.797**
NO_3^{-}				1	0.682	0	0	0	0	-0.138
Cl^{-}					1	-0.461*	0.146	0.27	-0.105	-3.80E-02
Pb						1	0.154	0.183	0.577	**0.883****
Cd							1	0.456	0.332	**0.99****
Cr								1	0.682	-0.191
Mn									1	0.405
Fe										1

Table 6: Correlation matrix for trace metals of groundwater samples in the area

Major Cations

Major cations spatial distribution maps were presented in Figures 3(a–d). Calcium variations is explained as the minimum, maximum, and mean values of 26, 155, and 74.11 mg/l, respectively (Table 5).

The elevated values of Ca2+ are found in the central parts of the area near industrial sites (Figure 3a) and this deviates from the general trend. According to Piper (1944), if $Ca^{2+}/(Ca^{2+}+SO_4^{2-})>0.5$ and TDS>500mg/l the source of Ca is carbonate dissolution/ from silicate minerals. In the study area $Ca^{2+}/(Ca^{2+}+SO_4^{2-})>$ is> 0.5 and TDS is > 500 in ELORA and Tannery well near the Sac and Plastic industry (Table 4 and Appendix 1). Therefore, in the study area in addition to hydrolysis of silicate minerals, the other reason for its elevated value might be from anthropogenic source (i.e., improper use and release of $CaCO_3$ tablet regents) /contaminated discharge of carbonates from Textile, Amir Sac and Plastic factory. The mean value of Ca^{2+} is within the permissible limit of (WHO, 2017) standards which is 200 mg/l.

The Mg^{2+} distribution map is also shown in Figure 3b with a mean value of 6.82 mg/l which is within WHO standards (150 mg/l). A higher value of Mg^{2+} was observed in northern and southwestern parts of the study area in which the area is dominated by basaltic rocks. According to Piper (1944), if $Mg^{2+}/(Ca^{2+}+Mg^{2+})$ is <0.5 (i.e., in the study area it is ≤0.29), Mg is supplied from the dissolution of altered ferromagnesian minerals (Appendix 1).

The Na^+ and K^+ concentrations are also shown in Figure 3(c and d) respectively. In the area 87.5% of water samples have TDS<500, and 93.8% have $Na^+/(Na^++Cl^-)>0.5$.

Based on Piper (1944), if $Na^+/(Na^++Cl^-)$ >0.5, the sources of Na are silicate weathering/sodium sources other than halite like albite and ion exchange conditions in thick clay soil. In some wells like ELFORA, the value of Na+ is highly increased. This is related to the infiltration of anthropogenic effluents like NaCl, Na_2SO_4 regents that used in ELFORA, and Na_2S regents in Tannery and Textile factory processing after they dissociate in to Na^+, Cl^-, S^{2-} when it comes in contacts with the soil moisture. However, 11.76% of water samples have <0.5 in $Na^+/(Na^++Cl^-)$ ratio, and TDS<500mg/l and the sources of these water samples are precipitation (Appendix-1, and Table 4). The value of K^+ is higher in wells in the eastern parts of the study area which is covered by Rhyolitic Ignimbrite. This indicates that, the origin of K^+ in water is often a result of chemical weathering and the subsequent dissolution of minerals from nearby silicate rocks and clay minerals.

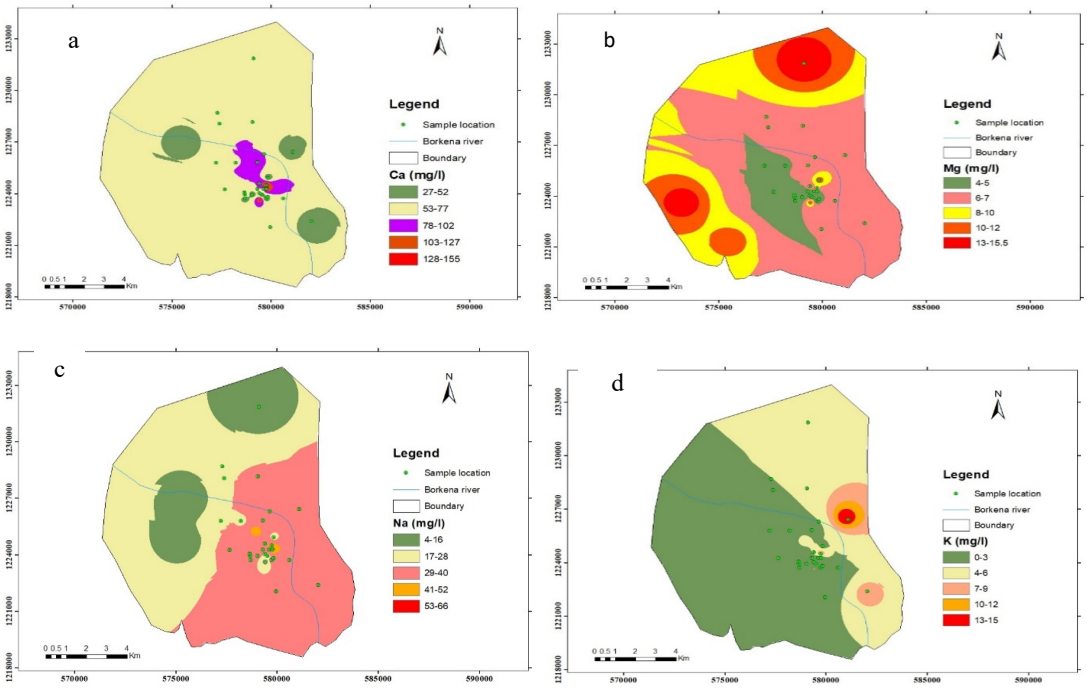

Figure 3: Spatial variation maps of major cations for the groundwater: Calcium (a), Magnesium (b), Sodium (c) and Potassium (d) of Kombolcha area

Major Anions

Bicarbonate (HCO_3-) which is the major anion is spatially distributed from lower values in the northern and southeastern direction to higher concentrations in the central, southwestern, and to some extent eastern parts (Figure 4a). The minimum, maximum, and mean values of HCO_3- are 1.2, 414, and 189.4 mg/l, respectively (Table5). Most of the samples (68.8%) are out of the range of (WHO, 2017) standard desirable limits which is 150 mg/l. If HCO_3-/sum of anion>0.8, the source of HCO3- is silicate weathering, and if <0.8 and sulphate is high, the source is gypsum/ carbonate dissolution (Piper, 1944). In the study area, 23.5% of water samples have>0.8 and 76.5% of the water samples have values <0.8 HCO_3/sum of anion ratio, and higher sulphate content. This indicates that both silicate weathering and contaminated carbonate dissolution from factories played a role in the increment of HCO_3- in the northern part of the study area

(i.e., non-polluted area) and central parts of the town (polluted zone) respectively (Appendix-1). Due to the use of $CaCO_3$ tablets as a reagent in the processing of the installed factories (i.e., Textile, and Sac and Plastic factories), there might be a contaminated discharge of carbonates from these factories, and this might have a significant effect on HCO_3- increment in some wells.

Sulfate (SO_4^{2-}) is the other anion that is important to be considered in the drinking water suitability analysis where more than 250 mg/l concentrations are not recommended. The minimum, maximum, and mean values that existed in the area are 1.8, 171.9, and 68.6 mg/l, respectively.

The most significant source of sulphate is pollution (Mohamed & Zineb, 2015). Dissolved sulphate has its origin from dissolution of sulphate contaminant from industrial discharges and intensive agriculture. Sulphate is also a major constituent in the aerosols which is from smoke coming from industries and automobiles (Dhakate & Lagudu, 2012; Mohamed & Zineb, 2015; Reyes et al., 2020). In the study area, higher sulfate might have also been derived from the leaching of sodium sulfate.

The maximum value is seen in shallow hand-dug wells like SW-1 and SW-2 where there are extensive agricultural practices, as well as nearby ELFORA and Tannery wells (Table 4) and (Figure 4b), because these wells are where Na_2S and Na_2SO_4 dissociate into Na^+ and S_2^- and Na^+ and SO_4^{2-} when they come into contact with soil or water, respectively.

The minimum, maximum and mean documented values of chloride (Cl^-) are 6.6, 38.7, and 21.7mg/l, respectively (Table 5). From the spatial Cl^- map indicated (Figure 4c), all its values are found below (WHO, 2017) standard. Even if it is below the standard, relatively higher values of Cl^- are highly related to industrial sites, urban centers, and irrigation/agricultural areas. If Cl-/Sum anions<0.8, the source is rock weathering or another factor (Piper, 1944). In the study area, the value is<0.8. This indicates rock weathering is the possible source (Appendix-1). Another anthropogenic factor, like domestic effluents, industrial effluents and immense agricultural practice may contribute to its increment in the study area due to an increase in value from the north towards the center of the study area.

Spatial concentration map of nitrate (NO_3^-) is shown in Figure 4d, and the minimum, maximum and mean value is found to be 3.5, 34.3 and 13.7 mg/l respectively. As indicated in the spatial concentration NO_3- map, all the value is within the recommended WHO limit. The concentration value increases in the urban centers. In Kombolcha town, the community used pit latrine and buried latrine pipes which are directly linked to surface water bodies. This and some other related domestic effluents cause the increment of NO_3-.

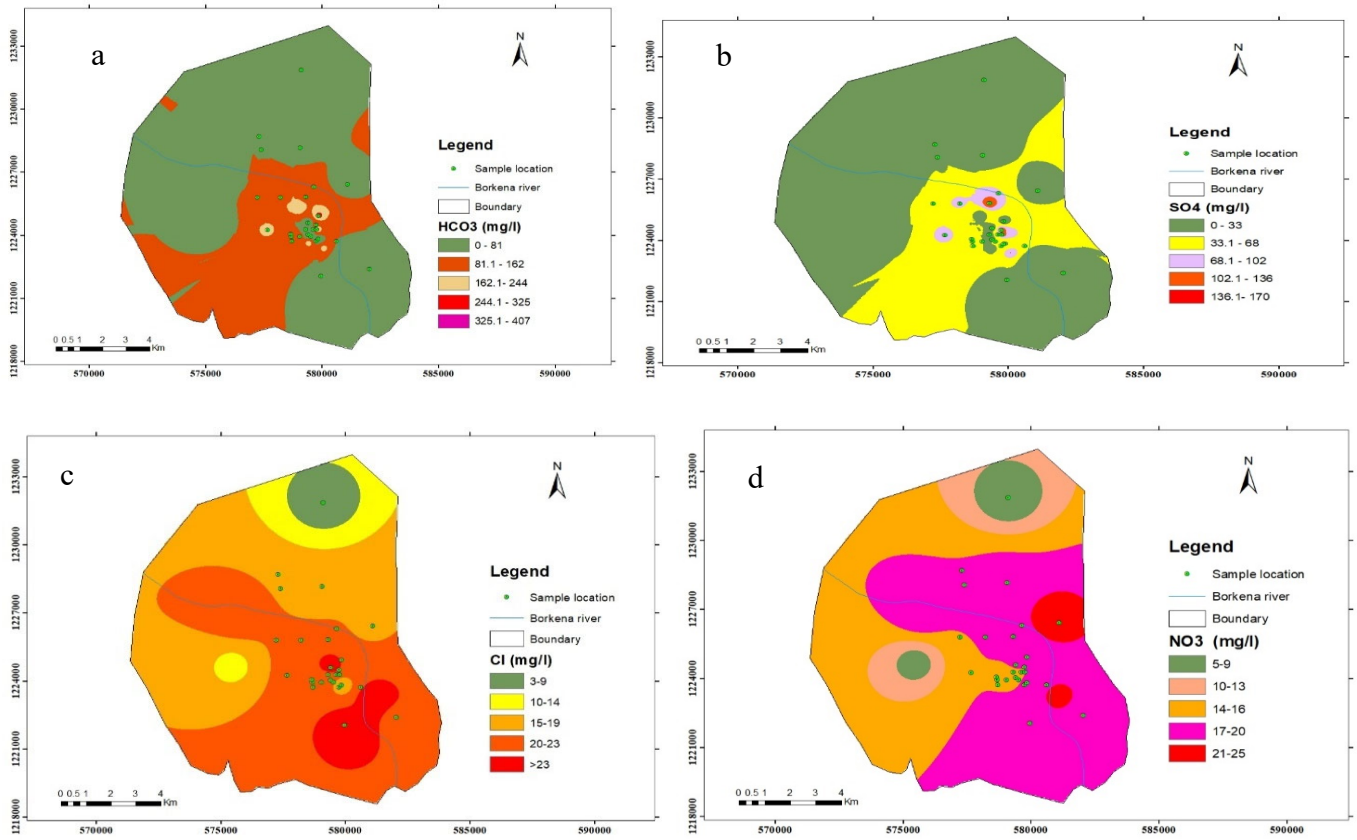

Figure 4: Spatial variation maps of anions for groundwater: Bicarbonate (a), Sulfate (b), Chloride (c), and Nitrate (d)

Heavy metals

Heavy metal spatial distribution maps for groundwater samples are presented in Figures 4(a–e). Cadmium (Cd) variations are explained as the minimum, maximum, and mean values of 0.002, 0.36, and 0.045mg/l, respectively. The elevated values Cd is found in the central parts of the area near Steel and Huaxu textile industrial sites (Figure 5a). The mean value of Cd is above the permissible limit of the (WHO, 2017) standard which is 0.003 mg/l.

The spatial variation of manganese (Mn), and iron (Fe) is shown in Figures 5(b, c) with the mean value of 0.259, and 0.422 mg/l respectively. The mean value of both Fe and Mn variables are above (WHO, 2017) standard limits which are 0.1 and 0.3 mg/l respectively. The groundwater with a higher value of Mn and Fe in spatial variation is closely related to the Steel and Huaxu textile factories (see the location of industries in Figure 1).

In the spatial map of lead (Pb), and chromium (Cr), the elevated values of the variables are closely related to hand-dug wells near Tannery and ELFORA (Figures 5d&e). The minimum, maximum, and mean values of the variables are 0.06, 1.071, and 0.146 for lead and 0.01, 1.032 and 0. 099mg/l for chromium. The mean value of both Pb and Cr are above (WHO, 2017) standard limits which are 0.01 and 0.005 mg/l respectively.

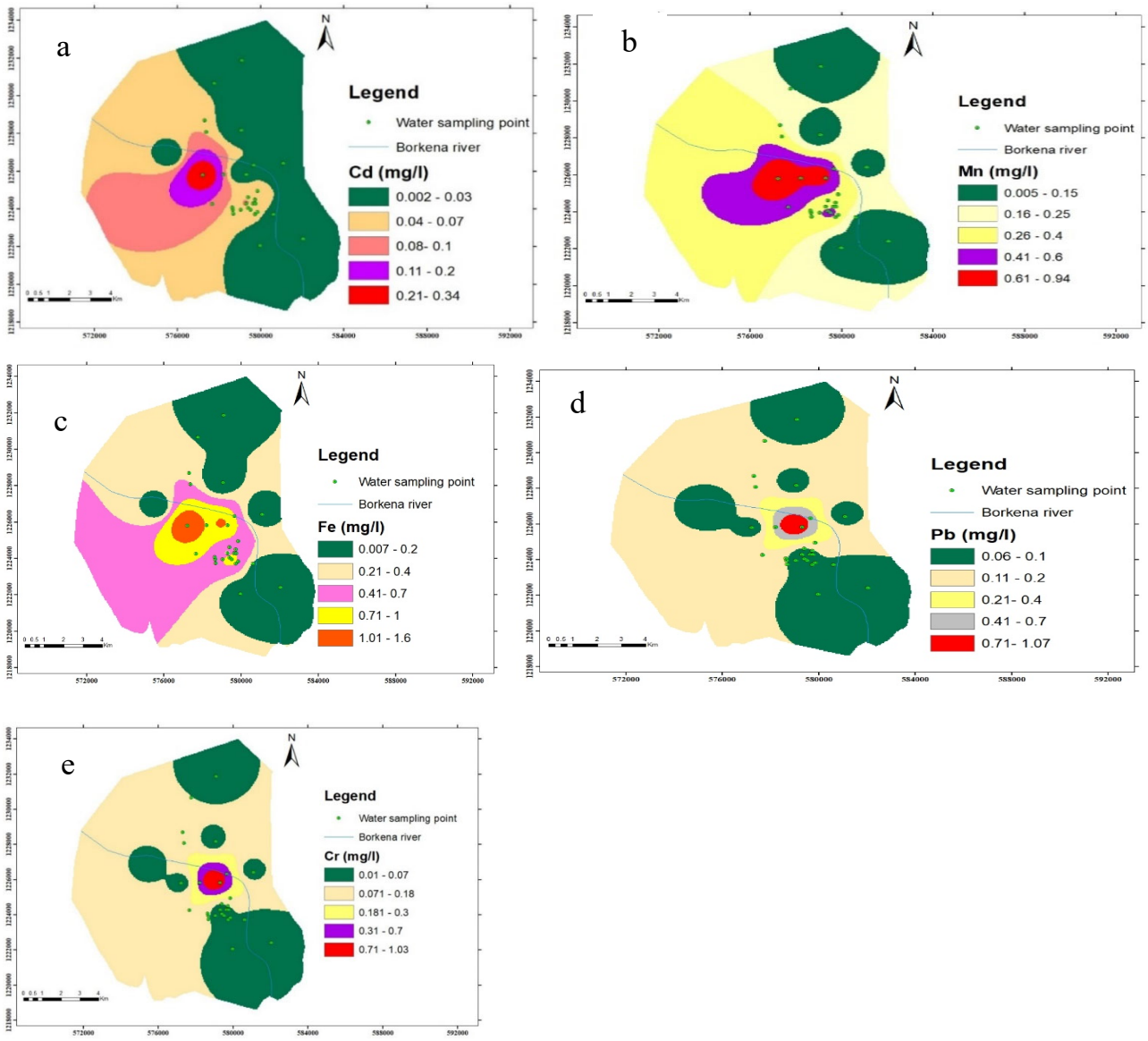

Figure 5: Spatial variation maps of heavy metals for groundwater: cadmium (a), manganese (b), iron(c), lead (d), chromium (e)

4.2. Pollution source identification and physicochemical variables of effluents

4.2.1. Principal component analysis (PCA)

Before PCA analysis, the Kaiser Meyer Olkin test (KMO) and Bartlett's test were performed on the data set. The KMO result was 0.651 and the Bartlett sphericity test was significant (.000, p <0.01), showing that PCA could be considered appropriate and useful to provide significant reduction in data dimensionality (Mustapha et al., 2011; Dwivedi & Vankar, 2014). PCA was applied on the data set to identify the spatial sources of pollution in in groundwater and Borkena River. According to Eigen value criterion, only PC's with Eigen value greater than one are

considered. According to the Kaiser criterion, only the first two factor groups could be used, because subsequent Eigen values are less than 1, the Scree plots is presented in (Figure 6). Two PC's were obtained with Eigen value greater than one with total variance of 84.3%, these are considered responsible for the variation in the groundwater, Borkena River and its tributaries system.

In the first principal component analysis, Mn, Fe, Cr, Pb, and Cd (in descending order)were found in amounts greater than 0.5 (Table 7), confirming that these metals were from anthropogenic sources. Since, manganese, iron, chromium, lead and cadmium are not found naturally in this region, enhanced concentration points forward towards industrial activities. After a survey of the industries found in Kombolcha, several iron, chromium, cadmium, carbonate, and lead- processing units were found to have been in operation for over 15 years, and aging machinery with inadequate controls could be sources of hazardous concentrations of heavy metals.

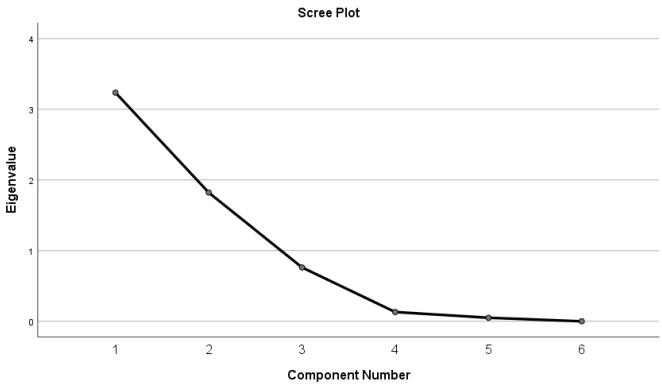

Figure 6: Scree plots for principal component analysis

Water quality parameter	PC1	PC2
Cl-	-0.480	0.896
NO_3-	-0.156	0.858
Fe	0.878	-0.185
Mn	0.892	-0.283
Cd	0.545	-0.112
Pb	0.646	0.401
Cr	0.651	0.401
Eigen value	3.235	1.821
% Variance	53.923	30.353
Cumulative variance	53.923	84.276

PC1, explaining 53.9% of the total variance, has strong positive loading on heavy metals Cd, Cr, Pb, Mn, and Fe. This result indicated that these metals originate from the same sources such as factories effluent process as described in Table 7.

PC2 explains about 30.4% of a variance, has strong positive factor loading on Cl- and NO3. This component group is typical of a combination of both anthropogenic and geogenic origins. The Cl-and NO3- is attributed to organic waste (domestic sewage) origin, and natural processes such as clay deposition and anoxic conditions of the aquifer, nitrification, and denitrification processes (Egbueri & Onitsha, 2020)

Different amounts of heavy metals like Fe, Cd, Cr, Cu, Zn,Pb, and physical parameters (measured in-situ) are released along with the industrial effluents (see Table 7).

A huge amount of Fe and Zn are discharged from steel factories. The greatest amount of chromium is discharged in Tannery industrial effluents and the concentration of lead is higher in Huaxu industrial effluents. A high percentage of the TDS is contributed by the steel industry, and the Huaxu textile industry. Also, the EC values are influenced by Steel factories, Tannery, and Huaxu textile industry influents. The extremely high value of pH is caused by Steel factory and Tannery factory effluents (see Table 7). By relating physicochemical variables of groundwater to the effluents, the pollution source was inferred. The all-over physicochemical variables of factories effluent samples in Kombolcha area are presented in Table 7. The pH of all effluent samples ranged from 8.2 to 12.8 with an average of 8.63, indicating that the effluent in this area was mainly alkaline. In the study area, TDS of industrial effluent varied with a wide range from 1331 to 3517 mg/l.

Therefore, for ground waters polluted by these trace metals, the causes are from a point source (i.e., effluents that contains Cd, Fe, Zn,Pb, and Cu). The main sources of pollution in the area are Steel, Textile, and Tannery factories. BGI brewery and ELFORA discharge heavy metal pollutants in small amounts relative to others (Table 8).

unit is in mg/l unless stated	Temp (0C)	pH	EC (µs/m)	TDS	Cr	Cd	Fe	Zn	Pb	Cu
Tannery (not working since mid-2019)	22.04	11.2	4160	2010	5.1	0.1	0.643	7.19	1.67	0.29
Huaxu Textile	24.95	9.55	3960	2422	0.4	0.5	3.68	7.19	3.3	0.29
BGI	23.7	8.3	2112	1770	0.03	0.08	0.79	0.072	0.15	0.2
Steel	21.3	12.8	4594	3517	0.0485	*	868.9	662.7	0.066	0.44
ELFORA	22.09	8.2	1740	1331	0.002	*	*	0.33	0.0049	0.16
*Represents no measured data										

Table 8: Chemical analysis and field measured results of factories waste water

4.2.2. Water quality index (WQI)

The computed WQI values and water quality classifications based on WQI ranges of the study area were presented in Table 9. From the table, the five WQI classes were obtained: Excellent water, good water, poor water, very poor water, and unsuitable water for drinking purposes.

From the total of 31 water samples, the majority of the samples (N = 19) comprised excellent to good water classes, which covers about 67.9% of the total samples. The next WQI water quality classes fall under poor to very poor water quality covering about 21.4% of the samples (N = 6). The remaining 10.7% of the samples (N=5) covers unsuitable/unfit water type for drinking. The spatial distribution map of groundwater using WQI value for the area is displayed in Figure 7. The majority of the area is mapped as excellent to good water type. Poor, very poor, and unfit water types are spatially distributed in the central parts of the area close to the factories. Of these samples (N=19), 46.4% (N=13) are below the (WHO, 2017) standard for each water variable and it is suitable for domestic consumption. 21.4% of samples (N=6), including KCTW-2R, BBH-s, KMIW, BH, and UBBH are above the standard limit with HCO3- and HD1 is above the limit with TDS, Fe, and Cd parameters. Even if it falls in excellent to good water types, these water samples are not suitable for domestic consumption.

No	Sample Id	WQI	Water type
1	BGI_1	37.73	Good water quality
2	BGI_3	36.31	Good water quality
3	BGI_4	38.29	Good water quality
4	ELF_W1	92.31	Very Poor water quality
5	Tex_W1	56.71	Poor water quality
6	Tex_W2	43.13	Good water quality
7	Tex_W3	40.03	Good water quality
8	Tex_W4	41.58	Good water quality
9	Tan_w	57.47	Poor water quality
10	KCTW_2R	50	Good water quality
11	SW_1	56.95	Poor water quality
12	SW_2	55.57	Poor water quality
13	BR_3	60.72	Poor water quality
14	BBH_S	17.17	Excellent water quality
15	KMIW	27.26	Good water quality
16	BH	24	Excellent water quality
17	UBBH	24.29	Excellent water quality
18	AHDW	29.62	Good water quality
19	BOSP	43.14	Good water quality
20	BR1	1753.04	Unfit /unsuitable for drinking
21	BUHD	37.11	Good water quality
22	HDBW	42.24	Good water quality
23	HD1	49.54	Good water quality
24	LSWJ	8742.77	Unfit /unsuitable for drinking
25	MHDW	45.11	Good water quality
26	TA1	144.06	Unfit /unsuitable for drinking

27	UBSP	23.34	Excellent water quality
28	BBH_P	36.21	Good water quality
29	BGI W	107.38	Unsuitable for drinking
30	BGI S	105.25	Unsuitable for drinking
31	SB	99.16	Very poor water quality

Table 9: Computed WQI of the study area and corresponding water quality classification

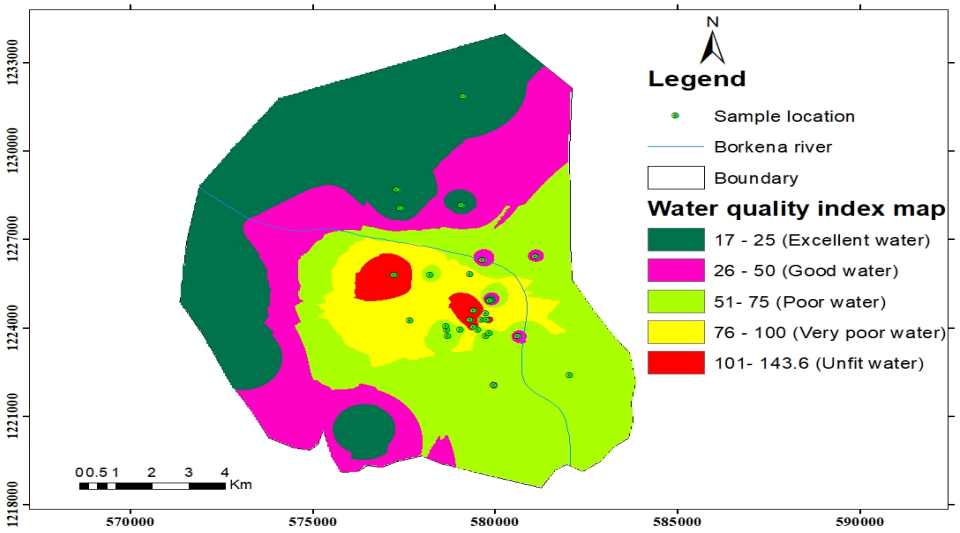

Figure 7: Spatial distribution map of WQI in the study area

4.2.3. Heavy Metal Pollution Index (HPI) of Groundwater

In pollution indexing, metals such as Pb, Cd, Cr, Fe, and Mn were considered. Heavy metal concentrations of groundwater and surface water samples, the guideline values, the maximum permissible (BIS, 2003), and desirable limit as defined by (WHO, 2017) were used. Descriptive statistics of the metal concentrations both in groundwater and surface water samples (in mg/l) were presented in Table 4 and 5 respectively. The computed HPI values and pollution level classifications based on HPI ranges from (Table 2), and (3) in the study area were presented in Table 8. As shown by the table, three HPI classes are obtained: low (<45), medium (45-90), and highly polluted (>90).

The HPI values for the study area were determined by incorporating the concentration values of recorded heavy metals. 41.7% of the groundwater samples had greater than the standard limit in Fe and Mn parameters. The detection limit of FAAS for Cd, Cr, and Pb are 0.002, 0.01, and 0.06mg/l respectively (see Table 1). In the study area, 66.7% of the groundwater samples had >0.002mg/l Cd. The amount of Pb and Cr in 75% of groundwater samples were less than 0.06, and 0.01mg/l, but it could be greater than the standard (WHO, 2017) limit (i.e., 0.01, and 0.005) respectively. The study used the instrument detection limit for HPI calculation and in descriptive summary statics of heavy metals. Based on HPI value 50.7% of the sample belongs to a low level of pollution, while 35% and 14.3% belong to a medium and high level of pollution respectively (Table 9). In the study, it is found that the mean metal concentration in groundwater is in the order of Fe>Mn>Pb> Cr> Cd. The mean concentration values of Fe, Pb, Cd, Cr, and Mn exceeded the drinking water standard (WHO, 2017).

In the present study, the concentration of iron ranges from 0.00754 to 1.586 mg/l with an average value of 0.42223mg/l (Table 5). The highest Fe concentration of 1.586 was found in the center of the studied area near the Steel industrial site. The lowest concentration of Fe was observed in the springs (i.e., UBSP) in the northern part of the studied area. The concentration of cadmium (Cd) for groundwater samples varies between 0.002and 0.36mg/l with an average value of 0.04475 mg/l (Table 5). All groundwater samples in the northern part of the study area had concentrations <0.002mg/l. The low values of Cd indicated that there is no significant source of pollution. The concentration of lead (Pb) in the study area varied between 0.06and 1.071mg/l with an average value of 0.14592mg/l. The concentration of chromium (Cr) ranged from 0.01to 1.032mg/l with an average value of 0.0995mg/l. In groundwater samples, the highest value of chromium with a concentration of 1.034mg/l was found near ELFORA and Tannery industrial sites. Also, the concentration of manganese (Mn) ranges from 0.00592 to 0.7421mg/l.

Sample Id	HPI	Level of water pollution
AHDW	37.06	Low
BOSP	38.12	Low
BR1	784.82	Highly polluted
BUHD	43.41	Low
HDBW	41.64	Low
HD1	81.24	Medium
LSWJ	1109.80	Highly polluted
MHDW	43.64	Low
TA1	89.65	Medium
UBSP	29.74	Low
BBH	40.52	Low
BGI W	83.17	Medium
BGI S	89.57	Medium
SB	56.11	Medium

Table 9: Computed HPI of the study area and corresponding water class

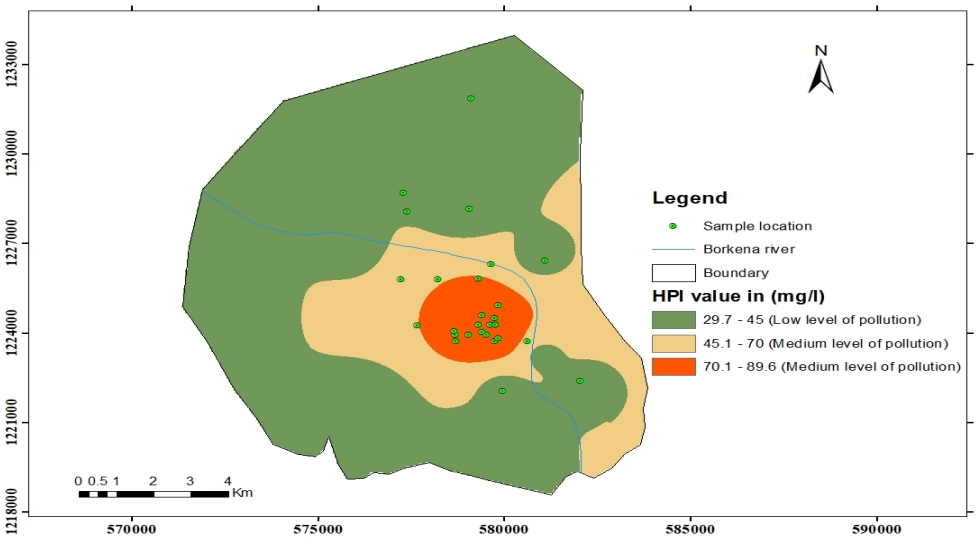

Figure 8: Spatial distribution map of HPI in the study area

5. Conclusion

The groundwater of Kombolcha city and its environment was analyzed and evaluated for its Heavy metal concentration and pollution status. All of the metals detected and evaluated had mean concentration above the required and permissible limit of WHO standards.

The multivariate statistical analyses (correlation, and principal component analyses) revealed that the release of heavy metals into the groundwater system is much more controlled by human (anthropogenic) activities than on natural (geogenic) processes. The result showed that among the variables studied heavy metals like Cd, Cr, Pb, Mn, and Fe are statistically the most significant parameters that bring variation in water quality in the area. The contribution of anthropogenic activities through discharge of industrial effluent into the groundwater and river is clearly identified by correlation matrix, concentration contour, spatial interpolation, and PCA. Based on the WQI value 67.9% comprised excellent to good water and the remaining 22.6% of the sample covers poor to unfit water types. HPI values revealed that all the groundwater samples in the area grouped under low to medium pollution level. The consumption of water with this elevated metal heavy concentration levels could result in health problems in individual taking such polluted water.

Author Contributions

The study conception, design, material preparation, data collection, laboratory analysis and original draft of the manuscript were performed by A.Y.A. A.B.N and A.E.A involved in writing, reviewing and editing the manuscript. All authors read and approved the final manuscript.

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Data Availability Statement: The data used in this study are

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Conflicts of Interest: The authors declare no conflict of interest.

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Appendix-1: Source-rock deduction summary from (Piper,1944)

Parameter	Value	Conclusion
HCO_3- /SiO_2	>10	Carbonate weathering
	<5	Silicate weathering
SiO_2/Na^++K^+-Cl^-	<1	Cation exchange
	>1 and <2	Albite weathering
	>2	Ferromagnesian minerals
Na^+/Na^++Cl^-	>0.5	Sodium source other than Halite- Albite, Ion Exchange
	<0.5, TDS>500	Sea water
	<0.5, TDS<500	Rain water
	=0.5	Halite solution
Mg^{2+} /Ca^{2}++Mg^{2+}	<0.5	Ferromagnesian minerals
	>0.5	Granite weathering
	=0.5	Lime stone- dolomite weathering
Ca^{2+} /Ca^{2+}+SO_4^{2-}	=0.5	Gypsum dissolution
	<0.5 and pH<5.5	Pyrite oxidation
	<0.5 and pH neutral	Calcium removal-ion exchange or calcite precipitation
	>0.5	Calcium source other than gypsum-carbonate or silicate
TDS	>500	Carbonate weathering or brine or seawater
	<500	Silicate weathering
Cl-/Sum Anions	>0.8 and TDS>500	Seawater or brine or evaporites
	>0.8 and TDS<100	Rainwater
	<0.8	Rock weathering or related factors
HCO3-/Sum Anions	>0.8	Silicate weathering
	<0.8, sulfate high	Gypsum/ carbonate dissolution
	<0.8, sulfate low	Seawater or brine