Research Article

Assessing the Industrial Effluent Effect on Irrigation Water Quality and Farm Soil near Kombolcha Town, Ethiopia

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This study evaluated various industrial effluents' effect on irrigation water quality and farm soil near Kombolcha town. Several industries such as brewery, steel iron, textile, and tannery have been installed near the Borkena River that crosses Kombolcha town. Representative samples of irrigation water and farm soil were collected from the upper and down part of Borkena river. The upper site was used as a control as it was not contaminated by industrial effluents. The analysis for selected parameters showed that the downstream irrigation water quality had mean concentrations of pH = 8.54, magnesium (Mg^{+2}) = 5.27 mg/l, carbonate (CO_3^{-2}) = 1.25 mg/l, bicarbonate (HCO_3^{-}) = 9.10 mg/l, copper (Cu) = 0.21 mg/l, chromium (Cr) = 0.31 mg/l, and cadmium (Cd) = 0.03 mg/l which were above the permissible limit of the Food and Agriculture Organization's (FAO's) irrigation water quality standard. The mean concentrations of electric conductivity (EC) = 0.96 ds/m, sodium (Na^{+}) = 3.35 mg/l, chloride (Cl^{-}) = 7.67 mg/l, and total dissolved solids (TDS) = 612.98 mg/l were slightly and moderately restricted for irrigation. Moreover, the concentration of heavy metals, calcium (Ca^{+2}) = 16.61 mg/l, iron (Fe) = 4.25 mg/l, manganese (Mn) = 0.18 mg/l, and lead (Pb) = 0.47 mg/l, was below the permissible limit of the FAO and nonrestricted. However, the mean concentration of EC, HCO_3^{-}, Cu, Cr, Cd, and TDS for downstream-irrigated farm soil samples was above the permissible limit of the FAO. The concentration of most selected parameters in downstream farm soil was also decreasing along with depth except pH, CO_3^{-2}, and HCO_3^{-}. Generally, there is a significant quality difference (at $P \leq 0.05$) between the upstream and downstream irrigation water quality on the parameters of Mg^{+2}, Cl^{-}, Pb, and Cu.

1. Introduction

Water is one of the most important natural resources essential for the survival of all living things including human beings. Irrigation is a vital use, but some dissolved or suspended substances found in water affect its suitability. The scarcity of surface and groundwater for irrigation is also an ever-increasing problem around the world. In many low-income countries, wastewater is discharged commonly into water bodies with little and no treatment as there are limited treatment facilities [1]. The use of wastewater for agriculture has become a common reality in three-fourth of the cities of Asia, Africa, and Latin America [2, 3]. In many parts of Ethiopia, there is a practice to use wastewater which is disposed to wells, ponds, streams, and treatment plants as a source of irrigation water [4, 5].

Due to the rapid population growth and the uncertainty over climate change, wastewater use in the agricultural sector may face many challenges. Long-term irrigation with poor-quality water damages the balance of nature, causing ecological deterioration on farmland [6]. The application of wastewater also significantly changes the soil's physical,

chemical, and biological properties [7]. Irrigation by effluents containing high salinity made soil secondary salinization easy and enhanced total alkalinity and sodium alkalinity sharply in the soil, causing soil hardening and soil permeability decrease [8]. The problem seems to exacerbate in the town, where farmland soil type is clay, compared to other types which state low-quality irrigation water is hazardous on clay soil [9, 10], while the same water could be used satisfactorily on the sand and/or permeable soils.

In Ethiopia, urbanization and industrialization are occurring rapidly throughout the year [11]. Due to the rapid increase in the urban population, urban agricultural activities are being recognized as an important source of food, nutrition, and income for the urban poor. However, irrigation is challenged with a lack of water, and the experience of using polluted rivers for irrigation is becoming a common practice near urban areas. In Kombolcha town of Ethiopia, the "Worka" and "Leyole" rivers, tributaries of the "Borkena" river, have been receiving untreated industrial effluents directly or indirectly, and local farmers are irrigating without any treatment. For instance, the electric conductivity (EC) for the steel processing effluent was found to be higher compared to the other industries (i.e., steel products industry = $4000 \mu S/cm$, textile industry = $800 \mu S/cm$, tannery industry = $2200 \mu S/cm$, and BGI brewery industry = $2100 \mu S/cm$) [12].

Moreover, results indicated that median concentrations of Cr in the tannery effluent and Zn in the steel processing effluents were as high as 26,600 and 155,750 $\mu g/l$, respectively, much exceeding both the United States Environmental Protection Agency (USEPA) and the Ethiopian emission guidelines. Cu concentrations were low in all effluents, whereas Pb concentrations were high in tannery effluents [12].

The quantification of the pollutants found both in irrigation water and farm soil is an important aspect. Additionally, more industries are being installed which will increase the amount of wastewater with high pollution load unless properly treated. There is no research done for the specified site in identifying the concentration of the pollutants both in irrigation water and farm soil. Hence, the main objective of this study is to assess the effect of industrial effluents on the quality of Borkena river irrigation water and farm soil for selected parameters.

2. Materials and Methods

2.1. Area Description. The study area is found near Kombolcha town located in the north-central part of Ethiopia placed immediately southeast of Dessie town in the Amhara Region. It is 377 km away from Addis Ababa (capital city) and is geographically located at $11^{o}06'$N, $39^{o}45'$E. River Borkena, which crosses the town, receives industrial effluents indirectly through its tributaries named "Worka" and "Leyole." Most of the industries are found close together in the middle of the town near the tributaries of Borkena (Figure 1).

The Kombolcha basin has a semiarid climate with an average annual rainfall of 1,030 mm, and the mean annual monthly temperature ranges from 24°C in January to 28°C in August. Kombolcha has two wet seasons, with the early wet season from February to April and later in the summer from July to September. The rains in the early wet season have been very low in recent years because of recurrent droughts with high annual potential evapotranspiration, reaching up to 3,050 mm/year in 2018. The rainfall in the wet season of June to September has remained relatively heavy and extensive (with a monthly average of 710 mm) compared with the early wet season (having an average rainfall of 130 mm) [13].

The landform of the study area includes rolling and undulating hills, with high plateaus to the west, the graben in the center, and the southward sloping ground to the Borkena River. The elevation of the land ranges from 1,750 m above sea level in the alluvial plain up to greater than 2,000 m above sea level in the uplands. Large parts of the built-up areas of the Kombolcha city have slope from 2.6% to 10%, and the slope of the hilly area increased to greater than 20%.

The local soils comprise alluvial/lacustrine deposits covering a large part of the town, with fluvisols at the banks of the tributaries of Borkena, colluvial screed deposits found mostly at the foot of hilly areas of the town and where Cambisols are developed, and Vertisol on the top of the alluvial or colluvial deposits, and covering most parts of the catchment areas [12].

2.2. Water and Soil Sampling Method. Samples of irrigation water and farmland soils were collected within one irrigation period, in three months, of the study area. Guidelines for Interpretation of Water Quality for Irrigation standard [14] and calibrated instruments were used during sample collection. Two sampling points, one in the upstream and the other in the downstream, were selected, i.e., upstream (A^*) Guragoye and downstream (B^*) Workiya, as shown in Supplementary Table S1. Composite water samples were taken from the two sampling locations, i.e., from the upstream and downstream of the Borkena River, between April and June. The intention was to characterize during the wet period (June) and the dry period (May). Representative soil samples were collected randomly using shovel slices at 20 different spots within the demarcated farmlands. One surface composite sample was collected in each irrigation phase, and a total of 3 composite surface samples were collected from the downstream-irrigated farmland. One composite surface soil sample from 20 different spots was collected for the upstream-irrigated farmland as the control. The samples were collected in a plastic bucket, and after thoroughly mixed, 0.5 kg of composite soil samples was used. Subsurface soil samples were collected from a 5 m × 5 m area by digging a V-shaped cut. Three pits were dug downstream of the farmland randomly, which is representative of the farmland soil sample. Nine soil samples were taken from the downstream-irrigated farmland in one irrigation phase within different depths (from 0 to 30 cm, 30 to 60 cm, and 60 to 90 cm). Totally, 27 subsurface soil samples were taken in three irrigation phases (one crop life) from the three pits' excavated area at the downstream irrigation farmland. Three subsurface
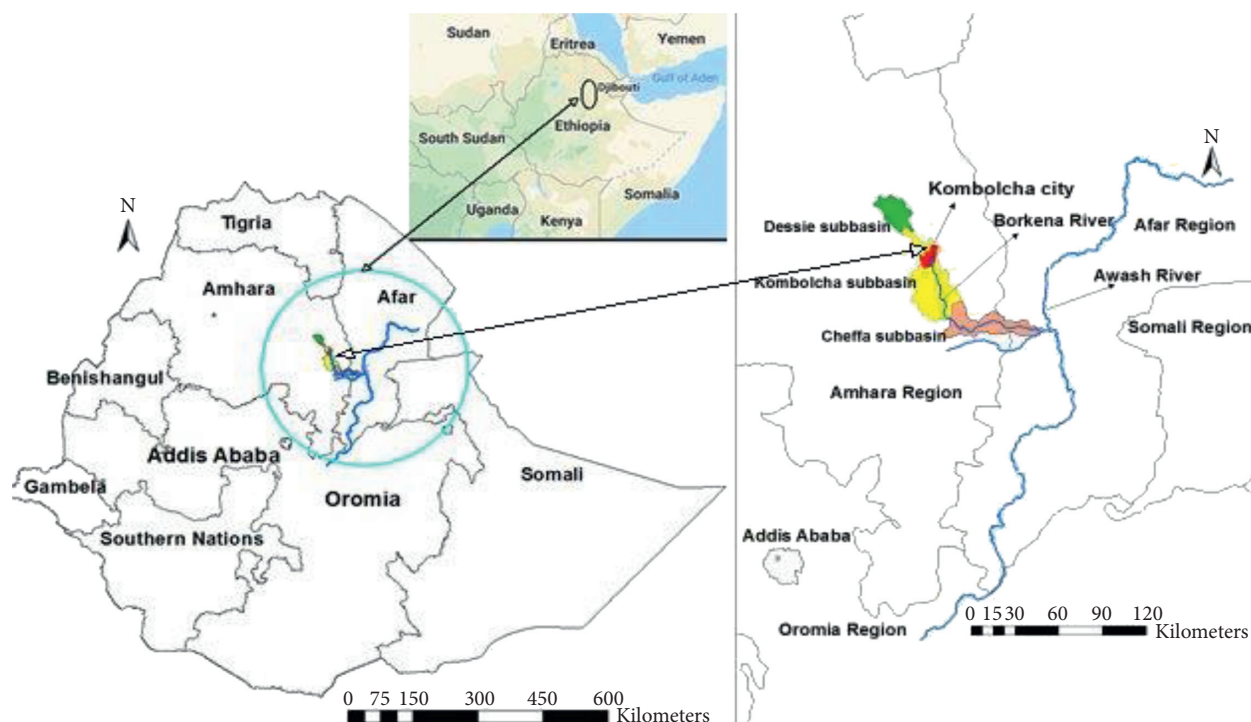
Figure 1: Location map of Kombolcha/study area.

soil samples were taken from the upstream-irrigated farm-land as a control in the 2nd irrigation phase. Finally, samples of 500 gm soil were collected at 30 cm intervals along with the depth. The summary of water and soil samples collected in the study area is presented in Supplementary Table S2.

2.3. Physicochemical Analysis of Water and Soil Samples.
pH, electric conductivity (EC), calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), chloride (Cl^-), alkalinity, and heavy metals were analyzed by following the standard procedures as outlined by USSL staff [15]. Total dissolved solids (TDS) and sodium absorption ratio (SAR) were calculated by formulas suggested in the FAO [14]. The physicochemical characteristics of the collected water samples were analyzed using the standard method [16]. The methods of physico-chemical analysis of water and soil samples are summarized in Table 1.

2.4. Statistical Analysis.
SPSS statistical software version 18 was used to determine the descriptive statistics to obtain the means, standard deviations, and coefficient of variances. The mean comparison was done using a t-test to find out whether there was any significant difference, at a 95% confidence interval, between the calculated means.

3. Results and Discussion

3.1. Chemical Characteristics of Sampled Water.
Physicochemical characteristics of downstream Borkena water quality in different irrigation phases and during the

dry and wet season are reported in Tables 2 and 3, re-spectively. Most of the parameter results were above the permissible limit of the FAO [14] standard (Table 4) except Ca^+, Fe, Mn, Pb, and SAR during April at different irrigation levels as there was no rainfall, but water sampled from the downstream of Borkena was below the permissible limit of irrigation water quality, in the wet (June) period, except for the concentration of CO_3^{-2} and HCO_3^-. The EC of down-stream Borkena irrigation water had 0.77, 0.67, and 0.68 dS/m and 1.25, 1.05, and 1.15 dS/m during wet and dry periods at different irrigation phases. High EC value is predominant with Na^+ and Cl^- concentrations [17]. The highest EC (1.15 dS/m) value was recorded during the dry period, and the lowest was 0.48 ds/m at the upstream which is below the permissible limit of the FAO. In general, downstream Borkena irrigation water exceeds the permissible limit of the FAO standard (Table 4).

As shown in Table 3, the mean values of CO_3^{-2} and HCO_3^- for downstream irrigation water were 1.75 mg/l and 10.22 mg/l during the dry period and 0.95 mg/l and 8.15 mg/l for the wet period. The results were above the permissible limit of the FAO's irrigation standard. High alkalinity concentration in irrigation water causes Ca^{+2} and Mg^{+2} ions to form insoluble minerals, leaving sodium as the dominant ion in the solution [18]. Mean pH at downstream Borkena irrigation water was 8.72 and 8.42 for dry and wet periods, respectively. The value of pH during the dry period was higher than the wet period (8.65–8.75), which is above the FAO irrigation water quality standard (6.5–8.4). High pH values are often caused by high CO_3^{-2} and HCO_3^- concentrations known as alkalinity [19, 20]. pH values of 4 or less and 12 or high cause death to most fish

TABLE 1: Methods for physicochemical analysis.

Analyzed parameter	Unit	Materials for test/method	Procedures
pH	—	Eco test pH meter/USEPA 8156	With the standard solution, calibrate at pH values 4.7 and 9.2
EC	ds/m	Conductivity Meter DIST 3 New	With the standard solution, calibrate using 0.01 N KCl
Ca and Mg^{+2}	mg/l	Titration/USEPA 8222	Using burettes, pipettes, and other volumetric glassware, standard solutions are prepared using analytical and distilled water
Cl^-	mg/l	Digital titration/USEPA 8206	Take 50 mL well-mixed sample adjusted to pH 7.0–8.0, and add 1.0 mL $K_2Cr_2O_7$
Na^+	mg/l	Flame photometer/1381-E	The characteristics of ions being determined by measuring the intensity of absorbance of light due to the electrons excitation
CO_3^{-2} and HCO_3^-	mg/l	Digital titration/USEPA 10244	The carbonate and bicarbonate effluent samples were determined by titrating with 0.03 N HCl
Heavy metals (Fe, Mn, Cu, Pb, Cd, Cr, and Ni)	mg/l	Atomic absorption spectroscopy/ USEPA 2201	Atomic absorption spectrometer
SAR	—	By using the formula SAR = (Na/ (Ca + Mg/2))	The values of Na^+, Ca, and Mg were obtained from the above and then calculated using the simple formula given here

Ca^+: calcium; Cd: cadmium; Cl^-: chloride; CO_3^{-2}: carbonate; Cr: chromium; Cu: copper; EC: electrical conductivity; Fe: iron; HCl: hydrochloric acid; HCO_3^-: bicarbonate; $K_2Cr_2O_7$: potassium dichromate; KCl: potassiumchloride; Mg^{+2}: magnesium; Mn: manganese; Na^+: sodium; Ni: nickel; Pb: lead; SAR: specific absorption rate.

TABLE 2: Physicochemical characteristics of downstream Borkena water quality in different irrigation phases.

Parameter	Unit	1st irrigation phase (April)	2nd irrigation phase (May)	3rd irrigation phase (June)	Mean
EC	dS/m	1.02	1.15	0.71	0.96
Mg^{+2}	mg/l	5.35	6.12	4.33	5.27
Ca^{+2}	mg/l	17.05	17.58	15.20	16.61
Na^+	mg/l	3.30	3.55	3.20	3.35
Cl^-	mg/l	5.00	8.00	10.00	7.67
pH	—	8.50	8.70	8.42	8.54
CO_3^{-2}	mg/l	1.05	1.75	0.95	1.25
HCO_3^-	mg/l	8.93	10.22	8.15	9.10
Fe	mg/l	4.13	5.12	3.50	4.25
Mn	mg/l	0.15	0.20	0.20	0.18
Pb	mg/l	0.49	0.53	0.40	0.47
Cu	mg/l	0.17	0.26	0.20	0.21
Cr	mg/l	0.40	0.50	0.03	0.31
Cd	mg/l	0.02	0.04	0.02	0.03
Ni	mg/l	< L.D	< L.D	< L.D	< L.D
SAR	mg/l	1.39	1.46	1.45	1.43
TDS		650.67	736.00	452.27	612.98

Ca^+: calcium; Cd: cadmium; Cl^-: chloride; CO_3^{-2}: carbonate; Cr: chromium; Cu: copper; EC: electrical conductivity; Fe: iron; HCO_3^-: bicarbonate; Mg^{+2}: magnesium; Mn: manganese; Na^+: sodium; Ni: nickel; Pb: lead; SAR: specific absorption rate; TDS: total dissolved solids; < L.D: less than the limit of detection.

species [21, 22]. The observed values reflected that downstream Borkena irrigation water is unsuitable for irrigation purposes.

The concentrations of heavy metals for the selected site are reported in Table 3. Results showed that higher concentration was recorded during the dry period except for Mn, and Cr showed high seasonal variation. The higher concentration of Fe, Pb, Cu, Cr, and Cd during the dry period might be due to no dilution as there is no rainfall. Similarly, Islam et al. [23] reported that Cd, As, Cr, Cu, Pb, and Ni are identified as the priority control metals. Therefore, this study provides quantitative evidence demonstrating the critical need for strengthened wastewater discharge regulations.

3.2. Characteristic of Water Quality Parameters in the Three Irrigation Phases. The result in Table 2 shows the physicochemical characteristics of downstream Borkena irrigation water. The samples taken in the 2nd irrigation phase had higher concentrations and were above the permissible limits of the FAO's standard. This is due to the lack of rainfall and industrial effluents released directly to the Borkena River without being diluted with rainwater. In the 3rd irrigation phase, water sampled from downstream Borkena was below the permissible limit of irrigation water quality except for the concentration of CO_3^{-2} and HCO_3^-. Minimum concentration was recorded in this period due to the dilution with rainwater, and the medium value was recorded in the 1st irrigation phase (Table 2).

TABLE 3: Physicochemical characteristics of downstream Borkena water quality during the dry and wet season.

| Parameter | Unit | Dry (May) period | | | | Wet (June) period | | | Mean |
		S_1	S_2	S_3	Mean	S_1	S_2	S_3	
EC	dS/m	1.25	1.05	1.05	1.12	0.77	0.67	0.68	0.71
Mg^{+2}	mg/l	6.25	6.05	6.05	6.12	4.55	4.25	4.20	4.33
Ca^{+2}	mg/l	17.25	17.75	17.75	17.58	15.00	15.25	15.35	15.20
Na^+	mg/l	3.55	3.50	3.50	3.52	3.25	3.15	3.20	3.20
Cl^-	mg/l	8.00	8.00	8.00	8.00	10.00	10.00	10.00	10.00
pH	—	8.75	8.70	8.70	8.72	8.45	8.40	8.40	8.42
CO_3^{-2}	mg/l	1.75	1.75	1.75	1.75	0.95	0.95	0.95	0.95
HCO_3^-	mg/l	9.95	10.25	10.25	10.15	8.25	8.05	8.15	8.15
Fe	mg/l	5.05	5.15	5.15	5.12	3.50	3.50	3.50	3.50
Mn	mg/l	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Pb	mg/l	0.55	0.50	0.50	0.52	0.40	0.40	0.40	0.40
Cu	mg/l	0.25	0.25	0.25	0.25	0.20	0.20	0.20	0.20
Cr	mg/l	0.50	0.50	0.50	0.50	0.03	0.03	0.03	0.03
Cd	mg/l	0.04	0.04	0.04	0.04	0.02	0.02	0.02	0.02
Ni	mg/l	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D
SAR	mg/l	1.46	1.43	1.43	1.44	1.47	1.43	1.45	1.45

Ca^+: calcium; Cd: cadmium; Cl^-: chloride; CO_3^{-2}: carbonate; Cr: chromium; Cu: copper; EC: electrical conductivity; Fe: iron; HCO_3^-: bicarbonate; Mg^{+2}: magnesium; Mn: manganese; Na^+: sodium; Ni: nickel; Pb: lead; SAR: specific absorption rate; TDS: total dissolved solids; < L.D: less than the limit of detection; S_1: sample 1; S_2: sample 2; S_3: sample 3.

TABLE 4: Mean values of irrigation water characteristics compared with the degree of restriction.

| Parameter | Unit | FAO degree of restriction (FAO Soil Bulletin 55, 1985) | | | Upstream Borkena | Downstream Borkena |
		None	Slightly restricted	Severe		
EC	dS/m	<0.7	0.7–3	>3	0.48	0.96
Na^+	mg/l	<3	3–9	>9	1.46	3.35
Cl^-	mg/l	<4	4–10	>10	5.07	7.67
Mg^{+2}	mg/l		Normal range: 0–5.0		2.18	5.27
Ca^+	mg/l		Normal range: 0–20		10.00	16.61
pH	—		Normal range: 6.5–8.0		8.38	8.54
CO_3^{-2}	mg/l		Normal range: 0–0.2		0.16	1.25
HCO_3^-	mg/l	<1.5	1.5–8.5	>8.5	4.76	9.10
Fe	mg/l		Normal range: 0–5.0		0.05	4.25
Cu	mg/l		Normal range: 0–0.2		0.06	0.21
Mn	mg/l		Normal range: 0–0.2		0.009	0.18
Pb	mg/l		Normal range: 0–5.0		0.28	0.47
Cr	mg/l		Normal range: 0–0.1		0.0045	0.31
Cd	mg/l		Normal range: 0–0.01		0.0089	0.03
Ni	mg/l		Normal range: 0–0.2		0.0034	0.0076
TDS	mg/l	<450	450–2,000	>2,000	305.07	612.98

Ca^+: calcium; Cd: cadmium; Cl^-: chloride; CO_3^{-2}: carbonate; Cr: chromium; Cu: copper; EC: electrical conductivity; Fe: iron; HCO_3^-: bicarbonate; Mg^{+2}: magnesium; Mn: manganese; Na^+: sodium; Ni: nickel; Pb: lead; SAR: specific absorption rate; TDS: total dissolved solids.

The average physicochemical characteristics of water from upstream and downstream Borkena are presented in Table 4. pH, both in upstream and downstream, was higher than the limit values; $Mg^{+2} = 5.27$ me/l, $CO_3^{-2} = 1.25$ me/l, $HCO_3^- = 9.10$ me/l, $Cu = 0.21$ mg/l, $Cr = 0.31$ mg/l, and $Cd = 0.03$ mg/l were above the permissible limit of the FAO's irrigation water quality standard. The mean concentration of $EC = 0.96$ ds/m, $Na^+ = 3.35$ me/l, $Cl^- = 7.67$ me/l, and $TDS = 612.98$ mg/l is a moderate restriction for irrigation, and the value of Fe is very close to the limit (Table 4). The others are below the permissible limit of the FAO's standard. However, prolonged application of this water under a poorly managed irrigation system could lead to the accumulation of these elements in the soil profile [23, 24].

Table 5 presents the t-test comparison of upstream and downstream water quality, and there were significant differences (at $p \leq 0.05$) for the mean concentration of Mg^{+2}, Cl^-, Pb, and Cu. However, there were no significant differences for pH, EC, Ca^+, Na^+, HCO_3^-, CO_3^{-2}, Fe, Mn, Cr, Cd, Ni, and TDS.

3.3. Levels of Pollutants in the Farm Soil. The physicochemical characteristics of sampled soils from the downstream of Borkena irrigated farmland in different irrigation

TABLE 5: Independent sample t-test for the upstream and downstream Borkena irrigation water.

Parameter	Unit	Upstream irrigation water	Downstream irrigation water	Levene's test for the equality of variance				t-test for the equality of means				
				Assumption of variance	F	Sig.	t	df	Sig. (two-tailed)	Mean difference	95% confidence interval of difference	
											Lower	Upper
EC	ds/m	0.48	0.96	Equal	7.08	0.76	−2.99	3	0.058	−2.00333	−4.1327	0.1261
				Unequal			−3.86	2	0.061	−2.00333	−4.2333	0.2266
Mg^{+2}	mg/l	2.18	5.27	Equal	9.6	0.53	−4.46	3	0.021	−4.70333	−8.0586	−1.3480
				Unequal			−5.76	2	0.029	−4.70333	−8.2172	−1.1895
Ca^{+2}	mg/l	10.00	16.61	Equal	6.11	0.90	−1.55	3	0.220	−8.26667	−25.2833	8.7499
				Unequal			−1.99	2	0.184	−8.26667	−26.0874	9.5540
Na^+	mg/l	1.46	3.35	Equal	3.34	0.17	−5.37	3	0.013	−26.1400	−41.6292	−10.6509
				Unequal			−6.93	2	0.020	−26.1400	−42.3610	−9.9189
Cl^-	mg/l	5.07	7.67	Equal	3.29	0.17	−3.58	3	0.057	−92.3366	−174.52	−10.1548
				Unequal			−4.62	2	0.044	−92.3366	−178.41	−6.2717
pH	-	8.38	8.54	Equal	5.66	0.98	−3.04	3	0.056	−0.55000	−1.1257	0.0257
				Unequal			−3.93	2	0.059	−0.55000	−1.1529	0.0529
CO_3^{-2}	me/L	0.16	1.25	Equal	8.57	0.61	−3.35	3	0.054	−1.09000	−2.1239	−0.0561
				Unequal			−4.33	2	0.049	−1.09000	−2.1728	−0.0072
HCO_3^-	me/L	4.76	9.10	Equal	3.97	0.14	−5.17	3	0.054	−15.5800	−25.170	−5.9895
				Unequal			−6.67	2	0.022	−15.5800	−25.6237	−5.5363
Fe	mg/l	0.05	4.25	Equal	2.73	0.19	−1.38	3	0.260	−3.31333	−10.92	4.2943
				Unequal			−1.79	2	0.215	−3.31333	−11.92	4.6537
Mn	mg/l	< L.D	0.18	Equal	9.60	0.05	−1.55	3	0.219	−0.01333	−0.0407	0.0140
				Unequal			−2.00	2	0.184	−0.01333	−0.4202	0.0153
Pb	mg/l	< L.D	0.47	Equal	6.54	0.08	−4.61	3	0.019	−0.7733	−1.307	−0.2396
				Unequal			−5.95	2	0.027	−0.7733	−1.3323	−0.2144
Cu	mg/l	0.06	0.21	Equal	3.94	0.14	−6.86	3	0.006	−0.20667	−0.3025	−0.1108
				Unequal			−8.86	2	0.013	−0.20667	−0.3071	−0.1063
Cr	mg/l	< L.D	0.31	Equal	3.57	0.16	−1.42	3	0.250	−0.0266	−0.0864	0.0330
				Unequal			−1.83	2	0.208	−0.0266	−0.0891	0.0358
Cd	mg/l	< L.D	0.03	Equal	9.60	0.05	−2.32	3	0.103	−0.0300	−0.0711	0.0111
				Unequal			−3.00	2	0.095	−0.0300	−0.073	0.1303
TDS	mg/l	305.07	612.98	Equal	7.08	0.08	−2.99	3	0.058	1282.13	−2644.92	80.652
				Unequal			−3.86	2	0.061	1282.13	−2709.31	145.845

Ca^+: calcium; Cd: cadmium; Cl^-: chloride; CO_3^{-2}: carbonate; Cr: chromium; Cu: copper; EC: electrical conductivity; Fe: iron; HCO_3^-: bicarbonate; Mg^{+2}: magnesium; Mn: manganese; Na^+: sodium; Ni: nickel; Pb: lead; SAR: specific absorption rate; TDS: total dissolved solids; < L.D: less than the limit of detection; F: statistics computed from sample variance for Levene's test; Sig.: significance; t: value of t-test (single value obtained after reduction of the entire sample by the t-test procedure); df: degree of freedom; Sig. (two-tailed): significance for two-tailed test.

phases and different depths are presented in Table 6. The average concentration of physicochemical parameters during the dry period (May) in the 2nd irrigation phase is higher than from the rain period (June). This is because industrial effluents are discharged without being diluted with rainwater and might be due to the weak adsorption nature in the soil. The concentration of pH, CO_3^{-2}, HCO_3^-, and SAR is increasing within the depth. However, the concentration of EC, Mg^{+2}, Ca^{+2}, Na^+, Cl^-, Fe, Mn, Pb, Cu, Cr, Cd, and Zn is decreasing along with the depth. This shows the movement of the chemical parameter, especially for heavy metals, is very slow, and the seepage level is minimal [25].

According to the FAO soil classification, soils showing EC < 0.7 ds/m, ESP < 15%, SAR<10, and pH from 6.5 to 8.5 are classified as normal soils. The average concentration of EC ranges from 0.8 to 0.9 ds/m during the dry period and from 0.6 to 07 ds/m during the rainy period but decreased along with the depth during the dry and rainy period. This shows that the EC of the downstream of Borkena irrigated farmland

soil is a moderate restriction for irrigation (i.e., above the permissible limit of the FAO). The CO_3^{-2} concentration ranges from 0.9 to 0.5 me/l during the dry and rainy periods which is above the permissible limit of the FAO. Generally, the concentrations of CO_3^{-2}, Cr, and Cd were above the permissible limit of the FAO. However, the average concentrations of Mg^{+2}, Ca^+, Na^+, Cl^-, pH, HCO_3^{-2}, Fe, Mn, and Pb were below the permissible limit of the FAO. Similarly, Kumar and Chopra [26] reported the increment of the concentrations of pH, EC, Cl^-, HCO_3^-, CO_3^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Zn, Cu, Cd, Pb, and Cr in the soil after irrigating with paper mill effluent for 12 weeks. Other studies also reported the increase in the concentrations of Ca, K, and Mg in the soil due to the wastewater application in irrigation [27, 28].

3.4. Effect of Industrial Effluent on the Irrigated Farm Soil.

As shown in Table 4, the salt concentration in the downstream of Borkena irrigation water was 0.96 ds/m which is a

TABLE 6: The characteristics of downstream Borkena irrigated farm soil during the dry and wet period.

Parameter	Units	1st irrigation phase (April)				2nd irrigation phase (May)				3rd irrigation phase (June)			
		Composite surface	Subsurface (cm)			Composite surface	Subsurface (cm)			Composite surface	Subsurface (cm)		
			0–30	30–60	60–90		0–30	30–60	60–90		0–30	30–60	60–90
EC	ds/m	0.8	0.8	0.7	0.7	0.9	0.9	0.8	0.8	0.7	0.6	0.6	0.6
Mg^{+2}	mg/l	4.6	4.3	4.0	3.6	4.8	4.7	4.6	4.5	4.1	4.0	3.9	3.8
Ca^{+2}	mg/l	17.4	17.2	16.9	16.5	18.6	18.6	18.3	17.8	17.1	16.8	16.7	16.3
Na^+	mg/l	19.8	19.6	19.6	19.3	21.9	22.2	22.1	21.5	19.0	18.8	18.6	18.1
Cl^-	mg/l	86.3	81.0	78.3	63.3	118.3	114.3	106.7	86.0	71.3	69.0	65.0	52.7
pH	0–14	8.5	8.6	8.6	8.6	8.3	8.4	8.4	8.4	7.9	8.0	8.0	8.0
CO_3^{-2}	mg/l	0.5	0.7	0.7	0.7	0.7	0.7	0.8	0.9	0.5	0.6	0.6	0.6
HCO_3^-	mg/l	9.4	9.7	9.9	8.8	11.5	11.9	12.1	12.0	8.5	9.5	10.0	9.7
Fe	mg/l	3.8	3.6	3.5	3.4	5.1	4.8	4.6	4.5	3.5	3.4	3.3	3.1
Mn	mg/l	0.1	0.1	0.1	0.1	0.3	0.3	0.2	0.1	0.1	0.1	0.0	0.0
Pb	mg/l	0.3	0.3	0.2	0.1	0.4	0.3	0.2	0.0	0.3	0.3	0.2	0.2
Cu	mg/l	0.2	0.2	0.1	0.1	0.3	0.3	0.3	0.2	0.1	0.1	0.1	0.0
Cr	mg/l	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1	0.1	0.0
Cd	mg/l	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D	< L.D
Ni	mg/l	0.1	0.1	0.1	< L.D	0.3	0.2	0.1	< L.D	0.2	0.1	0.1	0.1
TDS	mg/l	512.0	486.4	467.2	426.7	580.3	554.7	529.1	512.0	433.1	411.7	398.9	352.0

Ca^+: calcium; Cd: cadmium; Cl^-: chloride; CO_3^{-2}: carbonate; Cr: chromium; Cu: copper; EC: electrical conductivity; Fe: iron; HCO_3^-: bicarbonate; Mg^{+2}: magnesium; Mn: manganese; Na^+: sodium; Ni: nickel; Pb: lead; SAR: specific absorption rate; TDS: total dissolved solids; < L.D: less than the limit of detection.

TABLE 7: The characteristics of upstream and downstream Borkena irrigated farm soils.

Parameter	Unit	Upstream river water-irrigated soils in one pit				Downstream-irrigated farmland soils (mean value of three pits)			
		Composite surface samples	Soil profile samples (cm)			Composite surface samples	Soil profile samples (cm)		
			0–30	30–60	60–90		0–30	30–60	60–90
EC	ds/m	0.15	0.07	0.05	0.03	0.79	0.76	0.73	0.67
Mg^{+2}	mg/l	0.95	0.58	0.65	1.25	4.51	4.30	4.16	3.96
Ca^{+2}	me/l	15.00	14.75	12.25	13.55	17.68	17.51	17.26	16.87
Na^+	me/l	18.50	17.56	10.34	12.56	20.24	20.20	20.11	19.61
Cl^-	mg/l	62.00	60.00	55.00	50.00	92.00	88.11	83.33	67.33
pH	—	7.05	7.11	7.30	7.50	8.24	8.31	8.33	8.32
CO_3^{-2}	mg/l	4.35	5.00	4.35	4.00	0.57	0.66	0.72	0.74
HCO_3^-	mg/l	9.25	8.25	7.25	8.00	9.48	10.00	10.27	9.83
Fe	mg/l	< L.D	< L.D	< L.D	< L.D	4.09	3.93	3.77	3.66
Mn	mg/l	< L.D	< L.D	< L.D	< L.D	0.18	0.14	0.10	0.04
Pb	mg/l	0.10	0.10	0.10	0.00	0.32	0.28	0.22	0.09
Cu	mg/l	0.15	0.13	0.13	0.13	0.20	0.16	0.15	0.12
Cr	mg/l	< L.D	< L.D	< L.D	< L.D	0.17	0.15	0.14	0.12
Cd	mg/l	< L.D	< L.D	< L.D	< L.D	0.03	0.02	0.01	0.01
Ni	mg/l	< L.D	< L.D	< L.D	< L.D	0.20	0.15	0.08	0.06
SAR	mg/l	9.26	8.97	5.76	6.53	8.59	8.65	8.68	8.59
TDS	mg/l	96.00	44.80	32.00	19.20	508	484	465	430

Ca^+: calcium; Cd: cadmium; Cl^-: chloride; CO_3^{-2}: carbonate; Cr: chromium; Cu: copper; EC: electrical conductivity; Fe: iron; HCO_3^-: bicarbonate; Mg^{+2}: magnesium; Mn: manganese; Na^+: sodium; Ni: nickel; Pb: lead; SAR: specific absorption rate; TDS: total dissolved solids; < L.D: less than the limit of detection.

slightly moderate restriction on its use. In the case of the soil sample, the value of EC ranges from 0.67 to 0.79 ds/m. Therefore, based on EC values of irrigation water, it is a slightly moderate restriction for irrigation, and a moderate salinity problem was developed which required leaching. SAR (8.59 to 8.68) value of water in downstream Borkena irrigated farmland soil samples showed no restriction for use. Soils with SAR values greater than 10 are usually considered sodic. According to the FAO soil classification of the normal soil, as stated above, results of the downstream Borkena irrigated farmland soils are considered normal. Other studies reported that the accumulation in soil was insignificant compared to being added, and a difference might be only noticeable in the long term [29–32].

The mean value of physicochemical characteristics of the soil sampled in different irrigation phases in different sample stations from the upstream- and downstream-irrigated farmland is presented in Table 7. The result shows that the concentration of CO_3^{-2}, HCO_3^{-}, Cr, Cd, and Ni was above the permissible limit of the FAO and not suitable for irrigation. In the case of cations, Na^+ is the dominant ion followed by Ca^{+2} and Mg^{+2}. The concentration of pH, CO_3^{-2}, HCO_3^{-}, and SAR was increased, while the others decreased with depth. For this study, the order of heavy metals' concentrations is observed as follows: Fe > Cu > Pb > Cu > Mn > Cr > Cd > Zn. However, Marr et al. [33] reported Fe was the highest, while Cd was the least, Kumar and Chopra [26] reported the order of Pb > Cr > Cd > Zn > Cu after reirrigating with paper mill effluent for 12 weeks, and Tiwari et al. [34] reported the order of Fe > Mn > Zn > Cd > Cu > Pb > Cr > As after irrigating with industrial wastewater. The difference might be due to the differences in the wastewater characteristics used for irrigation and farm soil property. Generally, the long-term application of untreated and treated wastewater has resulted in the increment of pollutants in the soil [35–37].

4. Conclusions

The present study concludes that the industrial effluent drained to the Borkena River has affected the quality of irrigation water and farm soil. The river water quality of downstream showed higher concentrations of EC, Mg^{+2}, pH, CO_3^{-2}, HCO_3^{-2}, Cu, Cr, Cd, and TDS which were above the permissible limit of the FAO. Higher concentrations of heavy metals were also recorded during the dry period except for Mn, but Cr showed high seasonal variation. The soil analysis showed higher concentration of CO_3^{-2}, HCO_3^{-}, Cr, Cd, and Ni which was above the permissible limit of the FAO. In the case of cations, the dominancy is in the order of $Na^+ > Ca^{+2} > Mg^{+2}$. Along with the depth of the soil, the concentration of pH, CO_3^{-2}, HCO_3^{-}, and SAR increased, and the order observed for heavy metals was Fe > Cu > Pb > Cu > Mn > Cr > Cd > Zn. Generally, there are significant (at $p \leq 0.05$) differences for the mean value of Mg^{+2}, Cl^{-}, Pb, and Cu. The seasonal water application had some slight influence on soil chemical properties, i.e., the concentration of cations (Na^+, Ca^{+2}, and Mg^{+2}) was slightly lower than those in the dry period. Soils in the dry period, however, exhibited higher pH and HCO_3^{-} than those in the wet period. Hence, prolonged application of the polluted river under a poorly managed irrigation system could lead to the accumulation of these elements in the soil profile. To alleviate the problem, industries should be forced to treat their wastewater to the standard.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

Supplementary Materials

Supplementary Table S1: GPS coordinates of the sampling sites. Supplementary Table S2: summary of water and soil samples in the study area. (*Supplementary Materials*)

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