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Article

Impacts of Emerging Agricultural Practices on Groundwater Quality in Kahe Catchment, Tanzania

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Abstract: This paper assesses the impacts of farmers' intensive use of agrochemicals (fertilizers and pesticides) on groundwater quality in the Kahe catchment. Samples were collected during the wet and dry seasons of the year 2018 and analyzed for the presence of agrochemicals in the water. Groundwater chemistry was dominated by magnesium-sodium-bicarbonate (Mg-Na-HCO_3^-). The cations levels were in the trend of Mg^{2+} >Na^+ > Ca^{2+} > K^+, whereas anions were HCO_3^- > Cl^- > SO_4^{2-} for both seasons. The NO_3^- had an average value of about 18.40 ± 4.04 and 7.6 ± 1.7 mg/L in the wet and dry season, respectively. Elevated levels of nitrate, sulfate, phosphate, and ammonium were found in water samples collected near the large-scale sugarcane plantation in the catchment. For both seasons, Pb, Cd, Fe, Mn, Zn and Cu concentrations averaged approximately 0.08 ± 0.03, 0.11 ± 0.03, 0.16 ± 0.02, 0.11 ± 0.01, 0.46 ± 0.05, and 0.55 ± 0.02 mg/L, respectively. On the other hand, the concentrations were higher in shallow wells than in the deep boreholes. Pesticides' residues were below the detection limit in all sampled groundwater. The findings from this study provide important information for intervention in groundwater quality management in Kahe Catchment, Tanzania.

Keywords: intensive irrigation; groundwater quality; heavy metals; fertilizers; pesticides; Kahe catchment

1. Introduction

Groundwater is a vital water supply source to a community for different purposes in many sub-Saharan Africa countries [1]. It acts as an improved water supply in urban and rural areas so as to cope with surface water scarcity [2]. However, anthropogenic activities including agricultural practices, industrial effluents and inappropriate waste disposal on the land surface are considered to be major sources of groundwater pollution [3–5]. Recently, in agricultural fields, intensive use of agrochemicals (fertilizers and pesticides) have gradually increased in crop production worldwide [6]. To grow crops, large- and small-scale farmers use agrochemicals to increase their crop yields. As a result, they have increased their rates of fertilizers and pesticides applications, which could be impacting the groundwater quality. However, groundwater quality depends on different factors such as geological formation, soil type/soil permeability, the depth to the water table, the amount of rain and the hydraulic conductivity of the aquifer, and solubility of the rock materials within the aquifer system [7].

Degraded groundwater quality may present a public health risk given that the water is also being used by the households for their domestic needs. Globally, the use of fertilizers and pesticides is far higher than in Sub-Saharan Africa. For instance, the average application rate of fertilizers is reported to be about 19.3, 100 and 20 kg N/ha in Tanzania, Kenya and South Africa, respectively [8], while the global average is 220

kg N/ha [9]. The main risk of the increased application of agrochemicals by farmers arises from the apparent lack of knowledge on how, when, and what quantity to be used for a particular crop. It is likely that fertilizers and pesticides are being leached into groundwater systems through the intensification of irrigation and rainfall intensity [6,10]. Globally, this contributes about 70% of groundwater pollution [11], as several studies have shown in different parts of the world [10,12,13]. For instance, Rui et al. [14] argue that intensive fertilizer use has become one of the major sources of heavy metal contamination in groundwater around the agricultural areas. Numerous studies have reported on elevated levels of heavy metals in groundwater in agricultural fields in different parts such as in South West Bank, Palestine [15], in Lagos, Nigeria [16], in Hail region, Saudi Arabia [17], in Keko and Kigogo, Tanzania [18]. These include Pb, Zn, As, and Ni derived from inorganic fertilizers [19,20], or cadmium which is found in phosphate fertilizer [21–23]. Excessive use of the N-fertilizers is, therefore, a major source of groundwater nitrate pollution [13,24]. High levels of nitrate can lead to adverse impacts on human health such as methemoglobinemia for young children [24]. Past studies in Kahe catchment have concluded that the groundwater quality is still good [25,26], but recently reported agricultural land expansion in the catchment [26–29], increasing groundwater-based irrigation, may have impacted the water source. It is not yet well understood how the emerging use of fertilizers in the area contributes to nitrate pollution in groundwater. There is also limited information on the impacts of fertilizer use around agricultural fields in groundwater in the Kahe catchment.

Pesticides application has gradually increased in the agricultural fields in Tanzania; about 81% of pesticides are used in the livestock and agricultural area [6]. When the pesticides are used in areas with intensive irrigation or rainfall intensity, it is possible that they percolate through the soil and directly into groundwater [30]. According to Vrba [31], pesticides in groundwater are found in more than 20% to 25% of the agricultural areas in the Netherlands. In Tanzania, following mishandling at Vikuge farm (Kibaha), high levels of hexachlorocyclohexane (HCH) and dichlorodiphenyltrichloroethane (DDT) were recorded in sampled groundwater [32]. When pesticides surpass the recommended drinking water standards, they are linked to human health risks [33]. In the lower part of the Kahe catchment in northern Tanzania, one of the farms with intensive use of pesticides is Tanganyika Planting Company (TPC) for sugarcane plantation [34]. In Tanzania, several studies have reported pesticide pollution in surface water, soils and sediments [35–38]. For example, in the TPC farm area, about 90% of organochlorine pesticides were dominant in the soil [38]; while aldrin, dieldrin, heptachlor epoxide, HCH, endosulfan, and DDT were detected in surface water [39]. However, there is limited information regarding the presence of pesticide residues in groundwater.

In this study, it is examined whether the intensive agricultural practices through the use of fertilizers and pesticides to increase crop production is impacting groundwater quality in Kahe catchment. This area is well known for large scale irrigators such as TPC for sugarcane plantation, as well as small scales such as paddy rice, coffee, bananas, maize, onions, tomatoes, horticulture, and vegetables, which are all reliant on groundwater for crop irrigation. Groundwater samples collected from the area were analyzed for major dissolved cations, major dissolved anions, heavy metals, and pesticides. The findings provide useful information for sustainable management of the water resources in the Kahe catchment, as well as for future monitoring programs of the groundwater resources in the Pangani basin as a whole.

2. Materials and Methods

2.1. Study Area Description

Kahe catchment is one of the sub-catchments of the Pangani Basin located on the southern slopes of Mt. Kilimanjaro, in northern Tanzania (Figure 1). It has a total area of approximately 1038 km^2 [26]. The uppermost part of the catchment starts on the slopes of Mt. Kilimanjaro and ends at Nyumba ya Mungu dam. Meanwhile, the eastern and western part of the catchment is bounded by the Rombo and Hai districts, respectively. The area is characterized by semi-arid to Savannah climate and regulated by the intertropical convergence zone [26]. It receives a bi-modal rainfall with two peaks in March–June (long rain) and November−December (short rain). The annual rainfall on the southern slope of Mt. Kilimanjaro varies with

altitude where the maximum total rainfall of about 3000 mm/year occurs at an altitude above 2100 m amsl [40]. The lower elevation plains which are located below 1100 m amsl receive approximately 500–800 mm/year [40], while in the mid-level altitude of Mt. Kilimanjaro rainfall ranges from 1000 to 2000 mm/year [40]. The higher amount of annual rainfall occurs in the upper zone covered by natural dense forests. The annual air temperature in the catchment ranges from 15–36 °C, with June–August being the coldest months (15–23 °C) and January–February being the hottest months (32–35 °C) [26]. Furthermore, temperature decreases with increasing altitude where the mean annual temperature is 23.4 °C at an altitude of 813 m amsl, and 5.0 °C at 4000 m amsl [41].

The area is drained by several rivers including Karanga, Kikafu, Rau, Weru Weru, and Kikuletwa originating from the upper slopes of Mt. Kilimanjaro and Mt. Meru located in Arusha region (Figure 1). The rivers provide an estimated inflow to Nyumba ya Mungu dam of about 35–43 m^3/s [29], and a dam has a storage capacity of 870 million m^3 which supplies hydropower a total of 95 Megawatt (MW) in Tanzania [42]. The area above 1800 m amsl is reserved as natural forest zone and Kilimanjaro National Park (Figure 1), while human settlements and intensive agricultural practices based irrigation are in the lower elevation plains (900–1800 m amsl) [42]. The population growth, as well as the government and farmers investment in irrigated agriculture such as the lower Moshi irrigation scheme by Japan International Cooperation Agency (JICA), have contributed to the agricultural land expansion in the lower elevation plains of the Kahe catchment.

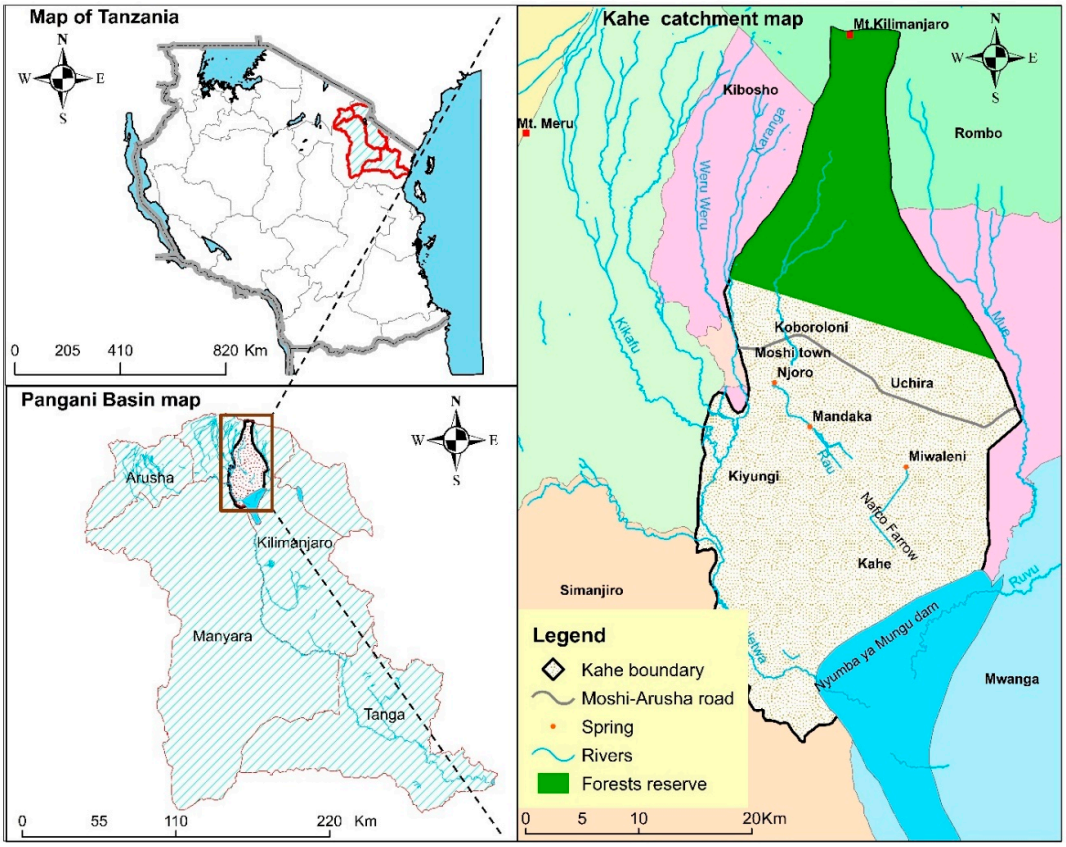
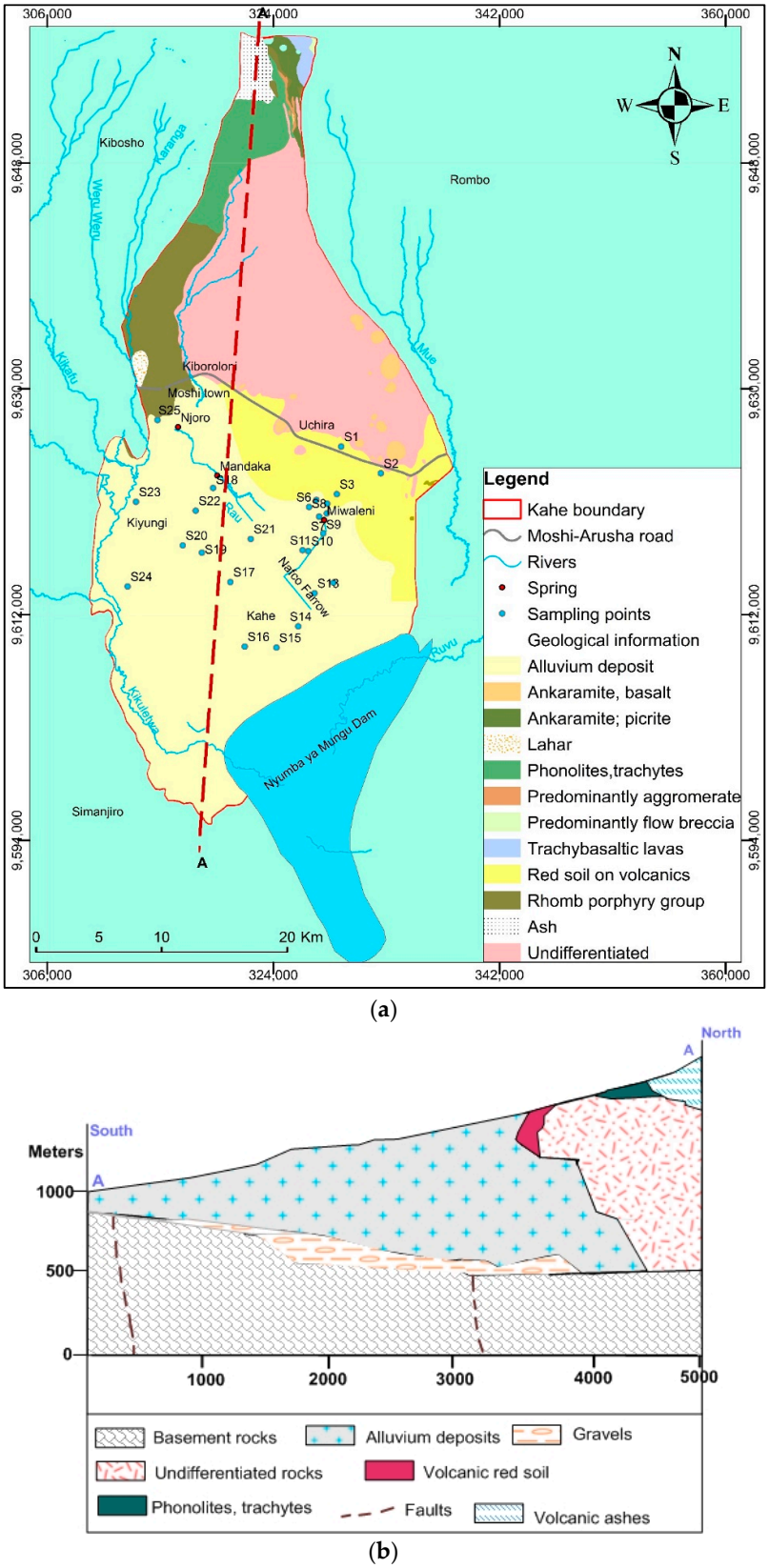


Figure 1. Study area map of Kahe catchment.

2.2. Geological and Hydrogeological Setting

The geological formation of the catchment starting from the center to the southern part of Moshi town is studded by quarternary superficial deposits of alluvium and Neogene superficial deposits of volcanic red soil derived from weathering of volcanic rock materials (Figure 2a). Mount Kilimanjaro is the major source of the volcanic activities in the Kahe catchment. These volcanic rocks are chiefly olivine, alkali basalts, phonolites, trachytes, nephelinites, and pyroclastics [43]. The alluvium deposits predominantly comprised sand, gravel, and clay, along with cancerous deposits with volcanic lava (basalts, trachytes) and pyroclastic volcanic rocks [26]. The cross-section showed that the layers are mostly unconsolidated (Figure 2b), its thickness is approximate >200 m at the center and becomes thicker towards north-east (NE) and shallow in the south near Nyumba ya Mungu dam [26]. The eastern part of the catchment, particularly north-east (NE) of Moshi-Arusha road, is covered by undifferentiated Neogene volcanic rocks (tertiary) that are related to the Shira eruptions. Shira volcanic eruptions produce volcanic rocks such as olivine, alkali basalts, trachybasalt, trachyandesite, basanite, and nephelinite, whereby they contain a wide variety of gravels materilas [26]. The western part is covered by Neogene phonolitic and trachytic rocks related to the Kibo and Mawenzi eruptions. The volcanic lavas (i.e., rhomb porphyry and trachyandesite group) were transported downward by rivers (Kikuletwa and Mue rivers) and deposited in the lower elevation plains. The Neogene volcanic rocks of rhomb porphyritic group including Penck rhomb porphyr and Weru Weru agglomerates extend towards the peak of Mt. Kilimanjaro (Figure 2a).

Kahe catchment is characterized as a fissured (residual soils on volcanic, undifferentiated rocks) and fractured volcanic hydrogeological aquifer [26]. Figure 2b shows that its formation was associated with limited faults which makes the basement rocks impermeable for a groundwater flow system [29]. Also, volcanic ashes and sedimentary formations, particularly fine-grained alluvium deposits, are characterized by low transmissivity which becomes practically impervious [44]. Groundwater recharge mainly takes place in high elevation on the slopes of Mt. Kilimanjaro along fractured formations as well as through infiltration. It has high conductivities, generally low groundwater tables, moderate topography, and porous aquifer media [26]. Groundwater potentiality in the fractured formation is also supported by a number of springs around the fault zone (Figure 2a). For instance, the area has the largest spring (Miwaleni spring) with a constant flow of 3–4 m^3/s [29], and the smallest springs including Mandaka and Njoro springs (Figure 2). The groundwater bearing formation lies between 2 and 60 m depths and deep wells had >100 m depth [26]. However, reliable information is required to demarcate the geometry of the aquifer; the wells used had limited hydrogeological data (well logs, depth, and specific yield) in the study.



(**a**)

(**b**)

Figure 2. (**a**) Hydrogeological map of Kahe Catchment; (**b**) hydrogeological cross-section A–A along the north–south direction.

2.3. Methods

2.3.1. Fieldwork and Groundwater Sampling

A handled global positioning system (GPS) device (Garmin Etrex 30xJ) was used to map the location of sampled shallow wells and the deep boreholes in the study area. A total of 25 wells were sampled: n = 4, deep boreholes with depth >100 m, and n = 21, shallow wells with depth <30 m (Figure 2a). Most of the shallow wells for irrigation are concentrated in the lower plains (900–1800 m amsl), where intensive agriculture is practiced by large and small scale farmers. The samples were collected during April–May 2018 (wet season) and September–October 2018 (dry season) in the study area. The groundwater samples were not collected in site locations above 1800 m amsl, the area characterized as natural forest zone and Kilimanjaro National Park (Figure 1).

The preliminary in-situ measurements of temperature, pH value, electrical conductivity, dissolved oxygen, and total dissolved solids were performed using multi-parameter HANNA instrument, Model HI 9828. The multi-parameter was calibrated before the measurement of the in-situ physical parameters using standard procedures recommended by the manufacturers [45].

Groundwater samples in open shallow wells were collected at least 50 cm below the water table using a bottle sampler, whereby, in closed deep boreholes the mixed water was collected after pumping for more than 20 minutes [46]. Groundwater samples were collected in clean 1 L HDPE plastic bottles for major ions analysis. For major ions and heavy metals including sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), iron (Fe^{2+}), zinc (Zn^{2+}), lead (Pb^{2+}), copper (Cu^{2+}) cadmium (Cd^{2+}) and manganese (Mn^{2+}) water samples were collected in clean 1 L HDPE plastic bottles and acidified using concentrated nitric acid, HNO_3 to a pH less than 2.0 [47]. Pesticides residue analysis water samples were collected using 1 L glass bottles and covered by black plastics to avoid rapid degradation due to a physical condition such as temperature and light intensity [48]. All samples were stored in a cool box containing frozen icepack and later transferred to the refrigerator at 4 °C at the laboratory.

2.3.2. Laboratory Analyses

(i) Major Cations and Trace Heavy Metals

All major cations Na^+, K^+, Mg^{2+}, Ca^{2+} and heavy metals Cu^{2+}, Fe^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Mn^{2+} were analyzed using atomic absorption spectrometer (AAS) PerkinElmer Analyst 100, in accordance with Standard Method for Examination of Water and Wastewater [47], to determine the concentration of each element in the sampled groundwater.

(ii) Major Anions

The concentrations of sulfate, nitrate, phosphate, and ammonium were determined according to the respective specified methods [49]: sulfate (SulfaVer 4 method) with SulfaVer 4 reagents, nitrate (cadmium reduction method) using Nitra Ver 5 Reagent, phosphate (ascorbic acid method) with Phos Ver 3 powder pillow, NH_4^+ (salicylate method) using ammonia salicylate and ammonia cyanurate reagent powder pillow. The HACH DR 2800 spectrophotometer was set and run at a specified shaking and reaction time as well as wavelength.

Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) were determined by titration method using standard sulfuric acid and Bromocresol green indicator solution [44]. Chloride (Cl^-) content was determined by argentometric titration method using standard silver nitrate ($AgNO_3$) titrant and potassium chromate indicator solution. Fluoride content was determined by the ion-selective electrode (ISE) method. These methods were realized in accordance with the Standard Method for Examination of Water and Wastewater [47].

(iii) Extraction of the Pesticides Samples

Unfiltered water samples were extracted by liquid–liquid extraction method (LLE) as described by [50]. About 500 mL of water samples were quantitatively transferred to a 0.5 L separating funnel and the bottle rinsed with ~30 mL of dichloromethane and combined with the water sample in the separating funnel. The combined contents were then successively extracted with dichloromethane three times (1 × 30 mL, 1 × 30mL, and 1 × 40 mL) with a total of 100 mL. The organic layer was filtered through a plug of cotton wool topped with anhydrous sodium sulfate Na_2SO_4 (~30 g) for drying and removing the impurities [50]. The combined extracts were concentrated in vacuo at 40 °C, and the final extract was made up in 2 mL ready for analysis using Gas Chromatography Mass Spectrometer (GC-MS).

2.3.3. Quality Assurance

Quality assurance was achieved by (i) calibration and verification of all instruments/equipment used, (ii) standardization and or checking efficiency and efficacy of all chemicals and reagents used, (iii) proper sampling and sub-sampling procedures (e.g., shaking) to ensure homogeneity of test samples [46], (iv) use of quality control samples prepared from certified reference materials, (v) determination of triplicate samples during on-site analysis and in-house analysis [47]. Data check accuracy for major constituents were computed by cations–anions charge balance [51].

2.3.4. Statistical Analysis

The statistical analyses were performed using Origin Pro 9.0 Lab software. The technique helps to understand the significant correlation of different parameters in a sampled groundwater by developing the correlation coefficients matrix. One-way analysis of variance (ANOVA-single factor) statistical test was used to compare all measured variables between a dry and wet season in Origin Pro 9.0 Lab software. For comparison, Alpha (α) = 0.05 is used to test for significance between the measured parameters in the wet season and dry season. Difference of the means is significant ($p < 0.05$) or not significant ($P > 0.05$). Multivariate statistical analysis technique, such as cluster analysis (CA) and principal components analysis (PCA), was performed using Paleontological Statistics (PAST) Software Package, Version 3.08 [52]. The technique was employed to understand the relationship between variables from different sampling sites and their relevance with respect to groundwater quality. Cluster analysis helps in grouping objects into classes (clusters) on the basis of similarities within a class and dissimilarities between different classes [53]. Moreover, to understand groundwater-chemistry composition for both shallow dug wells and deep boreholes in the wet and dry seasons, the analyzed sampled groundwater were plotted on the trilinear diagram as developed by Piper [54]. Basically, the trilinear piper diagram was designed for categorizing groundwater on the basis of chemical composition, and to compare chemical trends among different aquifer systems [51].

3. Results and Discussion

The complete sampled groundwater results for the wet season and dry season are presented in Appendix 1A and Appendix 1B, respectively. The analyzed groundwater parameters were compared to the recommended allowable drinking water Tanzanian Bureau of Standard [55] and international guidelines by WHO [24]. The summary of statistics including minimum, maximum, mean and standard deviation (SD) of the sampled groundwater are presented in Table 1.

Table 1. Summary statistics of measured variables in the sampled groundwater compared with drinking water guidelines.

	Wet Season				Dry Season					
Variable	**Min**	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**	**TBS (2016)**	**WHO (2011)**
PH	6.57	8.41	7.46	0.11	6.12	7.83	7.22	0.08	6.5–8.5	6.5–8.5
EC	158.6	1992	797.38	99.25	103.40	1294	598.43	64.90	1500	-

TDS	54	1186	459.76	56.91	187	1097	494.32	46.78	700	1000
Temp	21.9	27.8	24.7	0.27	22.3	27.7	24.9	0.30	-	-
NO_3^-	1.40	89.90	18.08	4.04	1.80	40.50	7.63	1.65	45	50
SO_4^{2-}	0.0	55.00	17.40	3.81	0.00	43.00	11.12	2.79	400	250
Cl^-	1.82	111.47	21.58	6.12	5.27	22.86	12.08	0.95	250	250
F^-	0.20	1.61	0.68	0.09	0.06	1.54	0.54	0.10	4	1.5
HCO_3^-	60	760	250.8	36.13	0	664	312.24	27.94	-	-
PO_4^{3-}	0.09	1.86	0.66	0.08	0.09	1.17	0.45	0.07	2.2	-
NH_4^+	0.01	0.32	0.14	0.02	0.01	0.41	0.13	0.02	2	-
Na^+	2.10	167.1	57.26	9.96	2.00	137.00	44.49	7.44	200	200
K^+	0.20	22.7	8.00	1.35	1.70	22.80	6.65	0.99	-	-
Mg^{2+}	2.20	256	86.21	24.59	4.40	165.40	39.16	8.32	500	-
Ca^{2+}	1.50	41.90	15.29	2.39	2.80	45.80	13.37	2.28	100	-
Fe^{2+}	0.03	0.59	0.17	0.03	0.03	0.39	0.14	0.02	1	0.3
Mn^{2+}	0.01	0.19	0.04	0.01	0.01	0.18	0.05	0.01	0.5	0.4
Cu^{2+}	0.00	0.53	0.11	0.02	0.00	0.15	0.06	0.01	3	5
Pb^{2+}	0.00	0.13	0.04	0.01	0.00	0.80	0.10	0.05	0.1	0.05
Zn^{2+}	0.12	2.57	0.66	0.07	0.04	0.66	0.31	0.03	15	5
Cd^{2+}	0.00	0.97	0.005	0.001	0.00	0.22	0.007	0.002	0.05	0.01

All units are in mg/l except pH (unitless), electrical conductivity (µS/cm), temperature (°C), SD—standard deviation.

3.1. Multivariate Cluster Analysis

Cluster analysis reveals the best results for interpretating four different groups of similarity between the twenty-five sampling sites referring to the different groundwater-quality parameters (Figure 3). The first group cluster A comprises a total of five samples which indicated similarity great than 93%; they are all located in the upper part of the catchment. For cluster A, four sampling sites (S01, S02, S03, and S05) out of five samples were collected from deep borehole water (>100 m) above 2000 m amsl. The second group (cluster B) comprised nine samples (S06–S14), and eight samples had >96% similarity index. Cluster C has a total of eight sampling sites all being a shallow well (<30 m), and two (25%) of its sub-clusters have greater than 98% similarity index. The final group (cluster D) has three sampling sites with great than 90% similarity both shallow groundwater as located in the western zone in a studied area. Generally, twenty-five sampling sites have revealed a similarity above 90% for all sampled groundwater in the dry and wet season.

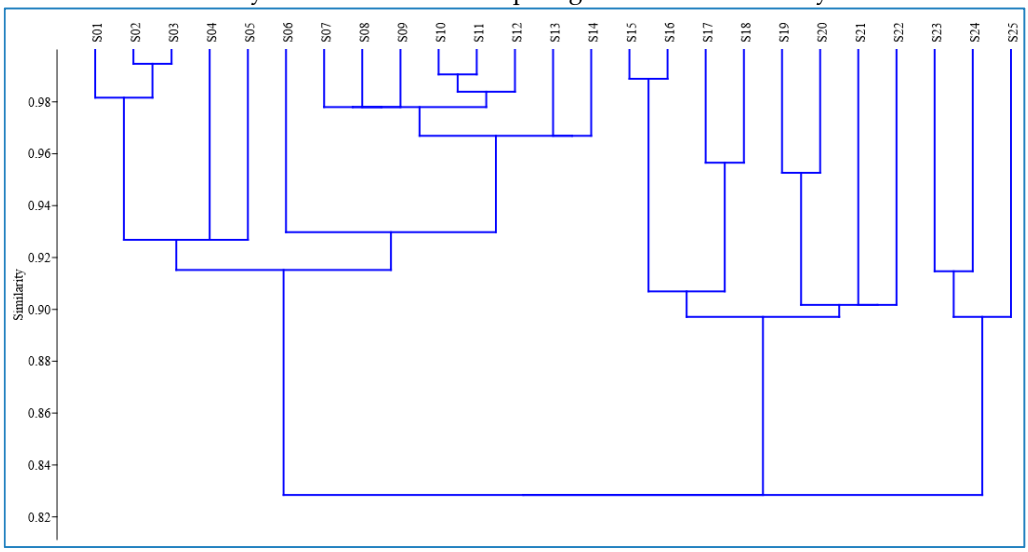


Figure 3. Dendrogram showing clustering of sampled groundwater.

3.2. Physical–Chemical Characteristics

Results of in-situ measurements are summarized in Table 1; the groundwater temperatures in the shallow wells and deep boreholes varied seasonally, but not significantly ($r(25) = 0.28$, $F = 0.858$, $p = 0.644$). Also, no positive correlation was found between the analyzed variables (Appendix 2A,B). It ranged between 22–27 °C, with an average value of 24.8 ± 0.29 °C in both seasons. However, sampled groundwater temperatures were almost similar with mean annual air temperatures 23.4 °C reported by [41]. Sampled groundwater was acidic to alkaline, as pH value varied between 6.12 and 8.41 for both seasons. About 24% of the water samples had pH < 7 in both seasons. However, all water samples were within the recommended value of 6.5–8.5 for drinking water guidelines [24,55].

The suitability of groundwater for drinking and irrigation purpose was indicated by the concentration of total dissolved solids (TDS) [31]. The average total dissolved solids were 459.76 ± 56.91 and 494.32 ± 46.78 mg/L in the wet and dry season, respectively. A value above 500 mg/L is undesirable for drinking water [56]. In the study area, the higher TDS concentration occurs in the western periphery, making the groundwater unsuitable for irrigation. For instance, in the western periphery near a shallow well (S07), the maize and tomatoes were not growing well relative to another area with a low value of TDS, especially the eastern part of the Kahe catchment.

The average electrical conductivity was 797.38 ± 99.25 μS/cm in the wet season and 598.43 ± 64.9 μS/cm in the dry season. The values were higher than the permissible value recommended by the World Health Organisation (WHO) [24]. It is found that electrical conductivity in sampled groundwater was proportional to the amount of total dissolved solids (Figure 4). There was significant positive correlation between EC and TDS with Pearson coefficients $r(25) = 0.92$, $p < 0.02$ for wet season (Appendix 2A) and $r(25) = 0.54$, $p < 0.01$ in a dry season (Appendix 2B). However, in most of the deep boreholes the TDS and EC values were within the recommended limits by in the WHO guidelines [24].

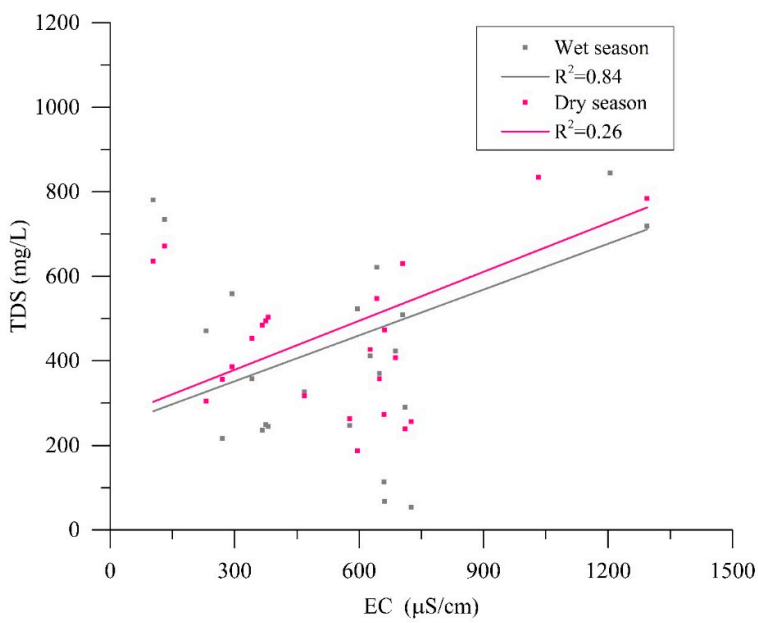
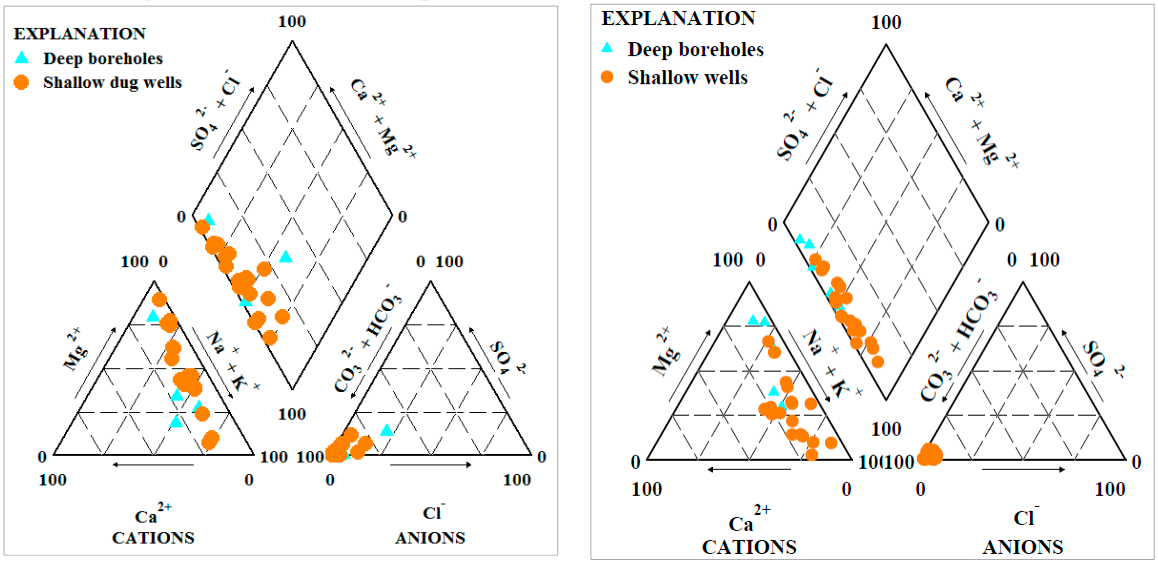


Figure 4. Relationship between total dissolved solids (TDS) and EC.

3.3. Major Ions in Groundwater

The major ions composition in studied groundwater is presented in piper diagram, in the wet season (Figure 5a) and in the dry seasons (Figure 5b). The analyzed water samples showed no significant difference in the cation and anion contents with respect to a depth between the wet and dry season ($p > 0.05$) (Table 2). There is statistically equal cation and anion concentration across all sampling depth in the Kahe catchment. Results show that groundwater chemistry is typically dominated by magnesium-sodium-

bicarbonate (Mg-Na-HCO_3^-) water type. Magnesium and sodium was abundant compared to other cations ($Mg^{2+} > Na^+ > Ca^{2+} > K^+$) in all groundwater samples. Elevated magnesium concentrations were 256 and 165.4 mg/L in the wet and dry season, respectively, while sodium had an average value of 57.26 ± 9.96 mg/L in the wet season and 44.49 ± 7.74 mg/L in the dry season (Table 1). The recorded high levels in the wet season are likely attributed to a cation exchange reaction between Na^+ and Mg^{2+} through water–rock interaction movement during the rainfall intensity events in the study area. Bicarbonate concentrations dominated more than other major anions ($HCO_3^- > Cl^- > SO_4^{2-}$) for both seasons. These have an average of 250.08 ± 36.13 mg/L in the wet season and 312.24 ± 27.94 mg/L in the dry season (Table 1). The major ions distribution (Figure 5a,b) and significant positive correlation (Appendix 2A) between bicarbonate ions ($HC0_3^-$) and cations were: (Na^+ r (25) = 0.53, p = 0.02), (Mg^{2+} r (25) = 0.33, p < 0.01), (Ca^{2+} r (25) = 0.67, p < 0.021) and (K^+ r (25) = 0.41, p < 0.019). The similar trend of significant positive correlation was observed in Appendix 2B. High bicarbonate levels in groundwater resulted from the reaction of carbon dioxide in the unsaturated soil zone and rainwater [57]. However, no literature documented the standard value of bicarbonate for drinking purposes, but a value above 200 mg/L is unsuitable for drinking water [58,59]. Overall, 36% of the sampled groundwater is permissible for drinking purpose. Generally, groundwater chemistry in the catchment is characterized by magnesium-sodium-bicarbonate water type. Similar findings have been reported the dominance of the sodium and magnesium in groundwater [44,60,61], as well as groundwater type in the Kilimanjaro aquifer [24], and Arusha aquifer [44] in Tanzania.



(**a**) (**b**)

Figure 5. Piper diagram for the chemical composition of groundwater for (**a**) wet season (**b**) dry season.

Table 2. One-way ANOVA single-factor results comparing major ions in the wet and dry season.

Parameter	df	F	p-value
Na^+	1[a], 48[b]	1.053	0.310
K^+	1[a], 48[b]	0.648	0.425
Mg^{2+}	1[a], 48[b]	2.506	0.120
Ca^{2+}	1[a], 48[b]	0.335	0.565
HCO_3^-	1[a], 48[b]	1.225	0.274
Cl^-	1[a], 48[b]	2.353	0.132
SO_4^{2-}	1[a], 48[b]	1.768	0.190

[a] Degree of freedom (df) between groups, [b] Degree of freedom (df) within groups.

The chloride (Cl^-) levels in the wet season varied from 1.82 to 111.47 mg/L with an average value of 21.40 ± 6.12 mg/L and in the dry season, it ranged from 5.27 to 22.86 mg/L and averaged 12.08 ± 0.95 mg/L. With the exception of two sites (S13 and S20), groundwater samples from all the 23 other sites had chloride

concentrations below 100 mg/L. The source of the Cl^- in groundwater is mostly from rainfall and sedimentary rocks with chloride minerals and irrigation processes [31]. However, chloride concentrations in the Kahe catchment in groundwater possibly come from the irrigation return.

Fluoride (F^-) in 23 of the sampled groundwater sources was within the limit of 1.5mg/L recommended for drinking water by WHO [24], while two samples S07 and S20 exceeded the value; all samples were within the Tanzanian standards [55]. The fluoride concentration varied from 0.20 mg/L to 1.61 mg/L and from 0.06 to 1.54 mg/L during the wet and dry season, respectively (Table 1). Its variation from one site to another is possibly associated with the geological formation (Figure 2a), which may have different dissociation rate, rainfall intensity, and cation exchange process in the aquifer system [44]. There was a significant positive relationship between F^- and K^+, r (25) = 0.57, $p < 0.01$) (Appendix 2A), and negative correlation with alkaline earth elements (Ca^{2+} and Mg^{2+}) (Appendix 2B). This correlation probably occurs through ionic exchange reaction and precipitation, when calcium and magnesium ion removed from the groundwater system additional K^+ and F^- ions are released from minerals such as nepheline in the aquifer materials. This study argues with several scholars who reported the relation between fluoride and alkali earth metals [62,63], as well as fluoride with bicarbonate (weak acid) [44]. The spatial distribution of fluoride concentrations indicates high fluoride concentration in shallow wells, i.e., at a depth 7–16 mn (cluster B and C), and lower values in deep boreholes (at a depth >100 m) for cluster A, but not significantly different with r (25) = 0.627, F = 1.215, p = 0.548 in both seasons in the area. In the study area, high fluoride concentrations in groundwater were likely due to the presence of basalt formation and other fluoride-rich volcanic materials such as lahars and volcanic ash (Figure 2a,b). However, groundwater quality for drinking purpose in the Kahe catchment is generally good, though in some areas it is considered not suitable for drinking purposes with elevated concentrations.

3.4. Seasonal Distribution of Nitrate, Sulphate, Phosphate, and Ammonium

In lower elevation plains around Mt. Kilimanjaro, high levels of nitrate (NO_3^-) in groundwater have been reported [25]. The sampled groundwater with relatively high $N0_3^-$ levels above 40 mg/L were from location S04 and S13; about 8% of the water samples (2 out of 25) exceeded the recommended WHO drinking water limit of 50 mg/L [24]. However, most of the water samples were recorded below 100 mg/L. From ANOVA one way analysis, results show that nitrate varied with depth, but not significantly at level p = 0.05, r (25) = 0.26, F = 1.35, p = 0.21 and r (25) = 0.32, F = 2.3, p = 0.15 in the wet and dry season, respectively. In shallow wells (at a depth below 17 m) the high content of NO_3^- was higher than in the deep boreholes for both wet and dry season (Figure 6). Similar studies reported the decrease of NO_3^- with respect to the depth due to intensive nitrogen fertilizer application in the agricultural field [64,65], while Scheytt [66] found that the nitrate concentrations decreased at depth 5–15 m below the ground surface. Nitrate concentrations in groundwater also varied seasonally, ranging from 1.4 to 89.9 mg/L and 1.8 to 40.5 mg/L in the wet and dry season, respectively. They were significantly different between the wet and dry season (r (25) = 0.36, F = 3.99, p = 0.051). The high recorded nitrate levels in the wet season likely of leaching of nitrogen fertilizers into groundwater through irrigation and rainfall intensity in a study area. This contradicts the study by Scheytt [66] reporting elevated nitrate around the agricultural fields during the rainfall events.

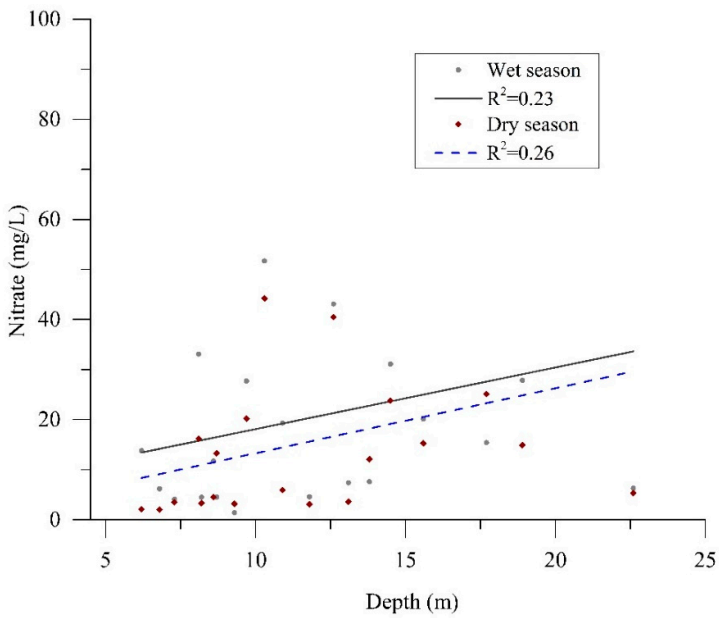


Figure 6. Nitrate variation with depth.

According to Patil and Patil [67] chemical fertilizers were among the major sources of phosphate level in groundwater. The results from this study showed that maximum values of PO_4^{3-} and NH_4^+ were 1.86 and 0.32 mg/L in the wet season, and about 1.17 and 0.41 mg/L, respectively, but all are within the permissible limit [55]. However, elevated levels of phosphate and ammonium noticed from cluster C (S20, S22) and cluster D (S24) out of twenty-five sample locations. There is a correlation between phosphate and ammonium, r (25) = 0.57, p = 0.005 in the wet season (Appendix 2A), and a partial linear relationship (Figure 7). The possible source of phosphate and ammonium in groundwater was attributed to intensive fertilizers use for crop production.

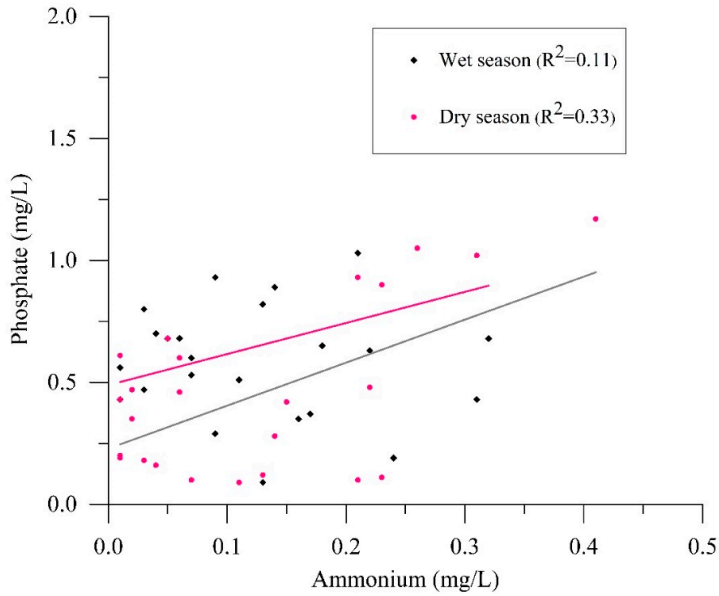


Figure 7. Relationship between phosphate and ammonium.

Sulphate (SO_4^{2-}) concentrations varied seasonally. In the wet and dry season sulphate concentrations were 17.40 ± 3.81 mg/L and 11.12 ± 2.79 mg/L, respectively, with a maximum value of about 55 mg/L and 43 mg/L (Table 1). Scheytt [66] showed that sulphate enriched in the soil through fertilizing infiltrates directly into groundwater. For instance, sulphur available in inorganic fertilizers generally exists as sulphate (e.g., ammonium sulphate) [68]. The high rate of SYNERGIZER fertilizer application possibly contributed to sulphate in groundwater in the area. Thus, measured elevated value may be associated with the recycling of irrigation water from agricultural practices instead of geological materials. Kahe catchment is comprised of volcanic rock and alkaline volcanic lavas such as pyroclastics (Figure 2a,b), where neither relate with metallic sulphide minerals reported as a major source of sulphate in groundwater [31]. In excess of 600 mg/L, it is linked to human health risk [24], such as in the gastrointestinal tract [24].

The raised values of nitrate, phosphate, sulphate, and ammonium in sampled groundwater were found near Tanganyika Planting Company (TPC) sugarcane plantation farm where intensive fertilizers have been in use since the early 1940s [34]. Also, there is a large number of small-scale irrigators for farming paddy rice, coffee, bananas, onions, tomatoes, horticulture, and vegetables, many of whom have increased their application of fertilizers for crop production. The source of elevated nitrate, sulphate phosphate and ammonium in the sampled groundwater nearby TPC sugarcane plantation farm in the western periphery in the Kahe catchment is therefore likely from the agricultural effluents.

3.5. Concentration Level of Heavy Metals in Groundwater

Groundwater was analyzed for the heavy metals Fe, Cu, Zn, Mn, Pb, and Cd in the wet and dry seasons. Significant differences between the wet and dry seasons are summarized in Table 3. The analyzed heavy metals are those that correspond to constituents from different fertilizers used by farmers in the Kahe catchment as derived from a field survey (Table 4). Most of the fertilizers applied were N-fertilizers as used for a sugarcane plantation, paddy rice, onions, watermelon, and tomatoes.

Table 3. One-way ANOVA, single-factor results comparing the wet and dry season.

Parameter	df	F	p-value
Fe	1[a], 48[b]	0.79	0.379
Mn	1[a], 48[b]	0.31	0.579
Cu	1[a], 48[b]	4.67	0.012
Pb	1[a], 48[b]	3.19	0.031
Zn	1[a], 48[b]	8.50	0.005
Cd	1[a], 48[b]	1.84	0.183

[a] Degree of freedom between groups, [b] Degree of freedom within groups.

Table 4. Types of fertilizers used in a studied area from field survey from the farmers.

S/No	Fertilizers	Ingredients	Constituents
01	Crop Wonder max	N.P.K (24:24:19)	Fe, Cu, Zn, Mo, Cd, and Mn
02	SYNERGIZER	N.P.K (8:32:4)	Mg, Fe, Pb, Mn, S, and Zn
03	BOOSTER	---	Mn, Fe, Pb, Zn, Cu and Cd
04	UREA $CO(NH_2)_2$.	N.P.K (46:0:0)	Fe, Pb, Zn, Cu
05	DAP $(NH_4)_2HPO_4$	18% N, 46% P_2O_5 and 20% P	----
06	CAN	Ca, NH_4 and N	----

In groundwater, heavy metals can occur naturally due to the dissolution of volcanic rock materials [69], but often in very low concentrations. Heavy metals contamination can also occur, however, from anthropogenic activities such as inappropriate disposal of wastes and industrial effluents, and application of agricultural fertilizers [70]. Either way, if the desirable drinking water concentration is surpassed, the metals can pose a serious human health problem. For example, a high concentration of dissolved iron can

cause liver disease (haemosiderosis) [31]. However, Fe is essential for the growth of animals and plants, and a shortage of Fe can lead to anemia [20]. Fe often occurs naturally in groundwater; high concentrations can be associated with the presence of igneous rock minerals. High concentrations can also result from the dissociation of the ferrous components of the borehole and hand pump [15]. Within the Kahe catchment, in both wet and dry season, the Cluster D (S22, S23, S24, and S25) in the west and sites of the Cluster B (S13) and Cluster C (S19) in the east had elevated levels of Fe, greater than 0.3 mg/L. Twenty out of twenty-five measured water samples (~80%) were within the allowable limits for drinking water as recommended by WHO [24]. Fe concentration varied seasonally, during the wet season with values higher than in the dry season (Figure 8). The high level of Fe in wet season is possibly influenced by rainfall infiltration and dissociation of iron mineral in rocks and soil which are leached into groundwater. A similar study found an excess of Fe in groundwater about 35% (wet season) and 7.7% (dry season) in Nigeria [71]. Also, Singhal and Gupta [72] found that in different parts of India with high rainfall, the Fe content was higher compared with low rainfall in groundwater.

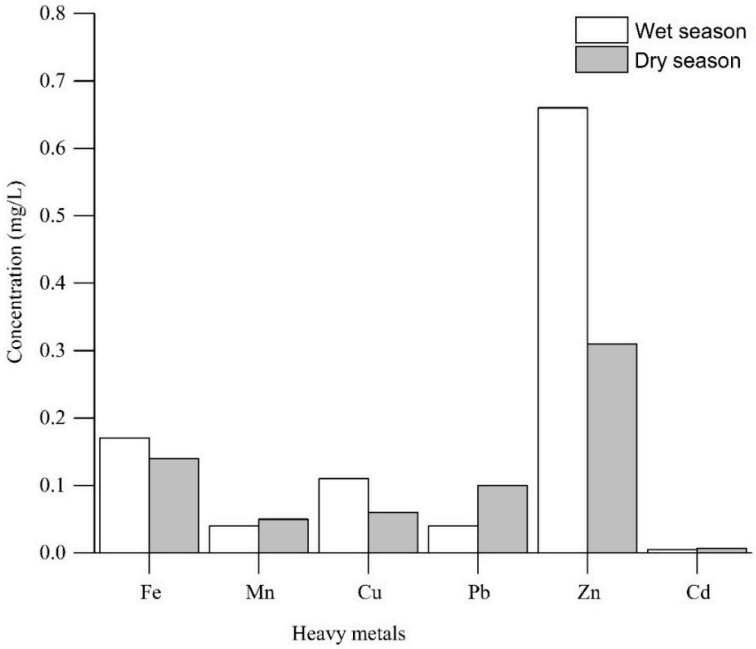


Figure 8. Average concentration of heavy metals.

Lead (Pb) is among the hazardous elements and in a human body causes problems such as anemia, hearing problems, kidney disfunction and blood pressure for both children and adults [24]. Lead concentrations in groundwater may occur from agricultural effluents with the excessive use of phosphate fertilizers [12,73]. About 24% of water samples (6 out of 25) were above the WHO permissible limits of 0.01 mg/L for Pb in drinking water [24]. Elevated Pb was noticed more in the dry season than in the wet season (Figure 8). In the dry season, Kahe catchment had intensive irrigation with the use of fertilizers for crop production. Phosphate fertilizers, e.g., DAP, are predominantly applied nearby TPC sugarcane plantation farm. The likely source of Pb in groundwater in the dry season was through irrigation return in the study area. In a similar study, in Keko (Tanzania), Mkude [18] found a maximum value of 0.35 mg/L (dry season) and 0.075 mg/L (wet season). Most of these shallow wells and deep boreholes were located within the agricultural field especially west–east zone as characterized by a concentration of large and small-scale irrigators. The maximum Pb value is obtained from the shallow well at site S23 near the TPC sugarcane plantation farm.

Zinc and copper are among the essential elements needed for plant and animal metabolism [74]. However, if available in excess then they become toxic to the human body. Zinc and copper in groundwater can originate from mining activities, metal plating and industrial effluents [3,75]. In the study area,

maximum Cu concentrations were 0.53 and 0.15 mg/L in a wet and dry season, respectively, while Zn was 1.57 mg/L in a wet season and 0.66 mg/L in a dry season (Table 1). Elevated values in the wet season may be from the dissociation of minerals and penetrate to groundwater during the rainfall events, but the source of Zn and Cu continue unrecognized in the area. However, Cu and Zn were within the recommended standard for drinking water guidelines [24,55]. Also, low concentration was likely due to the absence of the large industrial activities around the sampled groundwater sites. The Cu and Zn present were attributed to natural sources rather than anthropogenic activities. Generally, this study agrees with the results reported in different parts of the world [5,18,76,77] that show the lowest value of Cu and Zn in groundwater around agricultural fields.

Manganese has an average value of 0.04 ± 0.01 mg/L and 0.05 ± 0.02 mg/L in the wet and dry season, respectively. About 16% of Mn surpassed the recommended WHO guideline value (0.1 mg/L) (Table 1). There was a significant positive correlation between Mn with Zn $r(25) = 0.56$, $p = 0.005$ and with Cu $r(25) = 0.58$, $p = 0.002$ (Appendix 2A). However, the water samples of cluster C (S15, S19, and S22) show the maximum value of Mn in both seasons. The low concentration of manganese is possibly due to the absence of the large of industries in the area.

Cadmium (Cd) can be available in groundwater if an area was located around steel, plastic, and battery industries and through interaction with dissolved rocks and minerals [78]. The excess contents in drinking water cause kidney damage [24]. In studied groundwater, ANOVA at the 0.05 level does not show significant difference ($F = 1.84$, $p = 0.183$) in both the seasons (Table 3). However, elevated levels of Cd were recorded during the wet season at site S23. Generally, the shallow wells (<30 m) show higher concentrations of Cd than in deep boreholes (>100 m) for the sampled groundwater. The geological materials formation are alluvium deposits (Figure 2a,b), that are not possibly causing the occurrence of the Cd. Thus, the likely source of cadmium may be attributed to intensive use of fertilizers in the area through rainfall infiltration process. A study by Nouri et al. [5] reported the relation between the Cd and applied fertilizer (super phosphate) in Andimeshk aquifers, Iran. In the Kahe catchment, among the areas that use the phosphate fertilizer is especially the nearby sugar cane plantation farm in the western part.

3.6. Pesticide Residues

The analyzed pesticides residues are those that correspond to constituents from different types of pesticides used by farmers in the Kahe catchment as derived from a field survey (Appendix 3). Pesticide concentrations in the groundwater were below the detection limit (<1 part per trillion of Agilent 7800 ICP-MS). The undetected values of pesticides are presumably due to the small amount applied in the study area. Morris et al. [79] reported that high pesticide contents will arise from double or triple cropping and substantial applications of the same compound of pesticides. From the field survey, farmers reported that different types of pesticides were applied during crop growing period which reduces the threat of the contamination in groundwater. However, Leistra and Boesten [80] reported that the volatilization process may also contribute to the decline of the pesticides from the plant leaves especially if it is applied during daylight hours. Also, most of the pesticides can be attached to the soil particles as they are only slightly soluble in water and therefore are less likely to be found in the groundwater [24]. The rapid degradation of pesticide molecules is among the factors which contribute to reduced contamination of groundwater in the area. Sundaram [81] reported that for sub-surface soils, most of the pesticides get degraded within 14 days. For example, chlorpyrifos is degraded within approximately 10 days in a 0–15 cm and 40–60 cm clayey sandy soil. However, Rani et al. [82] found that pesticides exist in the top 10 cm of soil. For example, chlorpyriphos and cypermethrin were found distributed to a depth of 35 and 15 cm of soil, respectively. Their results indicate a low movement of pesticides under saturated moisture condition and hence may not contaminate groundwater.

4. Conclusion

Groundwater quality for drinking purposes in the Kahe catchment is generally good; however, in some areas it is considered undesirable for drinking purposes with elevated concentrations. Groundwater

chemistry was dominated with magnesium-sodium-bicarbonate water type. However, the major cation and anion concentration across all sampling depths was not significantly different in the study area. The agricultural practices likely had impacted on groundwater quality through the intensive use of fertilizers. For instance, elevated values of nitrate, phosphate, sulphate, and ammonium in sampled groundwater were found nearby Tanganyika Planting Company (TPC) sugarcane farm where the area had application of intensive fertilizers in the west zone of the Kahe catchment. Generally, shallow wells had higher values than deep boreholes. Pesticide molecules were below the detection limit in all the sampled groundwater, possibly due to the minimal amount applied or to degradation of molecules in the topsoil before reaching the groundwater.

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Conflict of interest: The authors declare that they have no conflict of interest.

APPENDIX 1A. Water quality parameter of groundwater for the wet season.

ID	Depth	P^H	DO	EC	TDS	Temp	$N0_3^-$	SO_4^{2-}	Cl^-	F^-	$HC0_3^-$	$P0_4^{3-}$	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{2+}	Mn	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cd
S01	120	6.57	4.74	378	245	24.3	3.5	1	9.13	0.22	90	0.43	0.01	2.11	0.21	17.8	2.40	0.08	0.02	0.03	0.02	0.31	0.002
S02	125	7.16	1.71	297	236	24.7	3.9	0	3.13	0.20	35	0.56	0.01	5	1.22	2.2	3.6	0.05	0.01	0.19	0.01	0.45	0.011
S03	118	6.72	4.13	382	249	24.7	9.2	0	6.78	0.24	55	0.47	0.03	6.7	1.7	6.4	4.1	0.17	0.02	0.05	0.01	0.92	0.004
S04	12.6	8.41	3.71	1290	781	24.1	43.1	51	76.42	0.87	84	0.51	0.11	115	8.1	57	29.4	0.11	0.03	0.01	0.02	0.58	<0.01
S05	115	7.21	1.17	664	357	23.2	4	1	3.91	0.33	85	0.35	0.16	5.3	1.9	12.6	3	0.10	0.02	0.06	0.04	0.17	0.002
S06	7.3	7.98	2.15	1687	735	25.1	4.1	48	30.78	0.71	1550	0.7	0.04	80.6	9.6	315	18.9	0.21	0.01	0.01	0.02	0.41	0.003
S07	6.8	7.82	3.46	1992	1186	25.4	6.2	32	13.30	1.57	544	0.93	0.09	75.5	22.7	74.2	19.1	0.15	0.05	0.04	0.03	0.39	<0.01
S08	6.2	7.28	4.11	903	471	23.1	13.8	5	6.26	0.32	100	0.43	0.31	11.2	3.6	15.2	5.3	0.13	0.02	0.18	0.02	0.83	0.003
S09	14.5	7.19	3.56	1344	845	23.7	31.1	0	11.74	0.41	206	0.6	0.07	28.4	1.5	119	8.3	0.12	0.03	0.01	0.04	0.74	<0.01
S10	8.2	7.91	2.86	509	327	24.3	4.5	4	6.78	1.03	192	0.68	0.32	21.6	5	2.6	6.7	0.17	0.05	0.21	0.02	0.63	0.001
S11	11.8	8.11	1.77	861	423	24.7	4.6	27	8.87	0.78	256	0.63	0.22	32.6	15.1	46.6	8.3	0.10	0.04	0.01	0.01	0.75	<0.01
S12	9.3	6.71	3.92	422	291	24.2	1.4	2	1.83	0.78	86	0.68	0.05	5.6	8.1	52.8	2.1	0.08	0.01	0.08	0.05	0.80	<0.01
S13	16.9	8.05	2.6	1196	719	26	89.9	12	111.5	0.59	334	0.89	0.14	130	13.9	53.6	32.6	0.37	0.02	0.10	0.08	0.33	0.012
S14	10.9	7.83	2.28	850	509	24.8	19.34	14	7.23	0.45	383	0.29	0.09	83.6	8.9	34.4	20.9	0.05	0.01	0.06	0.05	0.19	0.001
S15	13.8	8.02	7.35	158.6	113	23.5	7.6	2	6.1	0.38	625	0.09	0.13	121	12.9	49.7	30.2	0.07	0.02	0.09	0.07	0.29	0.002
S16	8.7	7.39	1.63	235	54	25.3	4.53	7	3.64	0.23	851	0.65	0.18	167	17.8	68.9	41.9	0.09	0.03	0.13	0.10	0.43	0.003
S17	10.3	6.69	1.88	949	216	24.6	51.7	0	30.51	0.57	1600	0.53	0.07	52.3	1.5	55.4	13.8	0.07	0.02	0.01	0.02	0.25	<0.01
S18	8.6	7.72	3.2	860	559	26	11.75	18	9.44	0.59	1261	0.68	0.06	24.1	0.7	256	6.4	0.03	0.01	0.04	0.01	0.12	<0.01
S19	9.7	7.41	5.2	291	68	27.8	27.7	55	21.39	1.30	270	0.82	0.13	93.7	12.9	14.2	22.8	0.32	0.13	0.02	0.01	1.91	0.001
S20	13.1	7.12	3.02	356	247	26.8	7.4	51	108.2	1.61	484	1.03	0.21	122	20.3	103	28.9	0.12	0.07	0.07	0.04	0.26	<0.01
S21	22.6	6.87	5.32	632	621	26.5	6.3	10	4.96	1.43	341	0.8	0.03	42.8	5.6	49	11.2	0.13	0.02	0.10	0.01	1.59	0.001
S22	15.6	7.8	1.36	527	371	21.9	20.11	31	16.09	1.04	896	1.86	0.28	114	14.9	131	29.8	0.23	0.19	0.27	0.03	2.57	0.003
S23	17.7	7.96	4.17	831	412	25.6	15.4	24	12.33	0.77	210	0.19	0.24	16.7	2.8	40.2	5.9	0.34	0.12	0.53	0.13	0.66	0.019
S24	8.1	6.97	3.91	1692	936	25.2	33.1	0	7.04	0.30	32	1.45	0.31	4.2	0.5	10.1	1.5	0.31	0.08	0.13	0.03	0.16	0.005
S25	18.9	7.48	1.54	628	523	22.8	27.84	40	22.29	0.36	464	0.37	0.17	70.9	8.5	70.8	25.1	0.59	0.03	0.25	0.01	0.80	0.007

All units are in mg/l except pH (unitless), EC (μS/cm), temperature (°C) and Depth (m)

APPENDIX 1B. Water quality parameter of groundwater for the dry season.

ID	Depth	P^H	DO	EC	TDS	Temp	$N0_3^-$	SO_4^{2-}	Cl^-	F^-	$HC0_3^-$	$P0_4^{3-}$	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{2+}	Mn	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cd
S01	120	6.82	1.16	381	503	23.5	6.2	0	11.88	0.15	400	0.68	0.05	2	2.1	24.8	2.9	0.07	0.03	0.01	0.03	0.11	0.001
S02	125	7.27	1.68	367	485	26.4	4.2	2	10.55	0.16	282	0.16	0.04	4.6	1.7	5.6	2.8	0.08	0.01	0.11	0.02	0.12	0.002
S03	118	7.23	1.80	375	495	23.1	5.3	0	19.21	0.10	500	0.35	0.02	6.6	4	6.2	4	0.03	0.02	0.03	0.01	0.32	0.003
S04	12.6	7.48	2.60	103.4	636	24.9	40.5	39	7.92	0.13	708	0.20	0.01	34	6.4	165	8.2	0.12	0.02	0.02	0.02	0.51	<0.01
S05	115	7.52	1.91	342	453	22.3	4	0	5.27	0.21	230	0.10	0.07	13.3	2.9	39.8	4.1	0.08	0.01	0.04	0.05	0.60	0.011
S06	7.3	7.64	4.53	130.6	672	26.7	3.5	3	18.47	0.70	365	0.18	0.03	38.1	6.2	41.8	9.8	0.07	0.03	0.09	0.03	0.42	0.005
S07	6.8	7.46	1.13	1225	1097	25.2	2	42	6.59	1.51	548	0.47	0.02	54.4	4	110	13.7	0.08	0.02	0.01	0.08	0.35	<0.01
S08	6.2	7.68	1.16	231.6	305	25.9	2.1	43	6.78	0.63	803	0.48	0.22	56	4.1	113	14.1	0.18	0.02	0.02	0.80	0.36	0.016
S09	14.5	6.79	1.03	1205	971	22.3	1.8	38	5.9	0.56	506	0.43	0.01	49.5	3.6	99.7	12.4	0.07	0.18	0.11	0.72	0.32	0.001
S10	8.2	6.69	1.96	468	318	26.2	3.3	0	11.87	0.91	86	0.28	0.14	16.1	3.7	4.4	6.8	0.13	0.02	0.04	0.01	0.27	0.011
S11	11.8	7.43	4.38	688	408	24.6	3.1	1	8.57	0.34	186	0.10	0.21	18.6	11	25.2	6.7	0.07	0.02	0.11	0.02	0.13	0.002
S12	9.3	7.68	4.53	711.6	239	25.4	3.2	9	9.23	0.56	252	0.60	0.06	4.3	8.1	31.6	3.5	0.08	0.03	0.01	0.01	0.30	<0.01
S13	16.9	6.41	3.78	1294	784	23.6	10.9	7	9.89	1.12	510	0.61	0.01	137	14.1	28.6	37.5	0.32	0.04	0.32	0.13	0.54	0.004
S14	10.9	7.61	1.49	705.2	630	25	5.9	8	7.74	0.14	305	0.09	0.11	62.7	6.7	33.9	4.5	0.06	0.05	0.06	0.15	0.04	0.005
S15	13.8	7.12	1.21	659.7	273	26.2	12.1	17	10.99	0.29	102	0.90	0.23	12.2	5.6	11.7	11.6	0.09	0.14	0.01	0.04	0.16	0.014
S16	8.7	7.83	2.62	725.5	257	24.8	13.3	9	12.08	0.18	504	0.19	0.01	67.4	17.2	44.9	45.8	0.13	0.03	0.02	0.16	0.66	0.001
S17	10.3	6.92	2.60	270	356	26.7	4.2	1	9.89	0.26	542	0.42	0.15	93.5	3.9	58.2	23.5	0.03	0.02	0.14	0.01	0.24	<0.01
S18	8.6	7.52	2.83	293.4	386	25	4.5	2	10.75	0.28	597	0.46	0.06	102	4.2	60.6	25.5	0.10	0.01	0.15	0.01	0.26	<0.01
S19	9.7	7.13	4.21	661.5	473	25.3	20.2	2	15.83	0.12	0	1.05	0.26	126	22.8	5.2	33.9	0.39	0.17	0.06	0.01	0.19	0.001
S20	13.1	6.57	3.40	577.8	263	24.9	3.6	4	17.07	1.54	134	0.93	0.21	42.5	3.4	9.6	12	0.09	0.02	0.03	0.02	0.42	<0.01
S21	22.6	7.3	3.78	642	548	27.7	5.3	8	13.19	1.14	223	0.12	0.13	39.2	5.6	16.2	13.5	0.08	0.01	0.01	0.01	0.32	0.021
S22	15.6	7.38	3.82	649	357	23	15.3	6	17.33	1.15	120	1.02	0.31	49.6	7.9	6.38	3.6	0.31	0.11	0.04	0.01	0.12	0.001
S23	17.7	7.12	3.69	626.2	427	27	25.1	9	22.86	0.11	116	0.12	0.13	28.2	3.1	15.8	13.1	0.29	0.09	0.02	0.11	0.21	0.022
S24	8.1	7.19	3.72	1032	835	23.2	16.2	16	12.99	1.12	95	1.17	0.41	38.6	7.2	5.9	8.3	0.33	0.11	0.01	0.03	0.32	0.003
S25	18.9	6.78	3.51	596.2	187	25.7	14.9	12	19.25	0.06	110	0.11	0.23	16.4	6.8	15	12.5	0.17	0.04	0.03	0.06	0.43	0.012

All units are in mg/l except pH (unitless), EC (μS/cm), temperature (°C) and Depth (m)

Negative correlation ($r < -0.5$); Deep pink, and positive correlation ($r > 0.5$); cyan colour.

APPENDIX 2A. Pearson correlation matrix of groundwater for the dry season.

	pH	DO	EC	TDS	Temp	NO_3^-	SO_4^{2-}	Cl^-	F^-	HCO_3^-	CO_3^{2-}	PO_4^{3-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{2+}	Mn	Cu^{2+}	Pb^{2+}	Zn^{2+}	Cd
pH	1																						
DO	−0.12	1																					
EC	−0.39	−0.36	1																				
TDS	−0.08	−0.37	0.54	1																			
Temp	−0.11	−0.09	−0.03	−0.31	1																		
NO_3^-	0.10	0.06	−0.18	0.01	−0.08	1																	
SO_4^{2-}	0.17	−0.60	0.26	0.45	−0.05	0.22	1																
Cl^-	−0.23	0.16	−0.16	0.31	0.24	0.00	−0.43	1															
F^-	−0.23	−0.36	0.47	0.35	−0.04	−0.22	0.21	−0.03	1														
HCO_3^-	−0.25	0.13	0.13	0.26	−0.23	−0.22	−0.08	0.15	0.50	1													
CO_3^{2-}	−0.39	−0.20	0.55	0.13	0.03	0.00	−0.13	0.20	0.39	0.11	1												
PO_4^{3-}	−0.28	−0.19	0.30	0.04	−0.31	0.15	0.03	0.12	0.41	0.02	0.25	1											
NH_4^+	−0.13	−0.13	0.08	−0.28	0.03	−0.02	−0.08	0.28	0.22	−0.31	0.24	0.57	1										
Na^+	−0.13	−0.43	0.28	0.22	−0.01	0.20	0.03	−0.10	0.15	−0.12	0.49	0.26	0.01	1									
K^+	0.10	−0.14	0.30	−0.06	−0.07	0.41	−0.13	0.09	0.58	0.40	−0.44	0.25	0.16	0.57	1								
Mg^{2+}	0.31	−0.48	−0.09	0.38	−0.06	0.35	0.80	−0.57	−0.02	0.65	−0.36	−0.23	−0.41	0.16	−0.15	1							
Ca^{2+}	−0.08	−0.47	0.26	−0.02	0.10	0.20	−0.01	0.02	−0.02	0.58	0.43	0.10	−0.12	0.79	0.68	0.08	1						
Fe^{2+}	−0.20	−0.15	0.33	0.06	−0.16	0.32	−0.01	0.39	0.15	−0.20	0.62	0.52	0.52	0.44	0.55	−0.26	0.35	1					
Mn	−0.21	−0.23	0.44	0.21	−0.26	0.19	0.19	0.13	−0.05	−0.44	0.24	0.54	0.40	0.20	0.33	−0.14	0.12	0.51	1				
Cu^{2+}	−0.18	−0.33	−0.01	0.00	−0.01	−0.05	−0.04	−0.15	−0.14	−0.27	−0.13	0.08	−0.02	0.55	0.01	0.19	0.33	0.09	0.20	1			
Pb^{2+}	0.11	−0.62	0.39	0.48	−0.10	−0.25	0.81	−0.43	0.27	−0.01	−0.08	−0.04	−0.17	0.15	−0.14	0.61	0.09	−0.07	0.15	0.06	1		
Zn^{2+}	0.05	−0.31	0.04	0.06	−0.18	0.19	−0.68	−0.09	0.15	0.29	0.15	−0.18	−0.33	0.15	0.18	−0.50	0.43	0.02	−0.27	−0.20	0.12	1	
Cd	−0.06	−0.17	−0.09	−0.28	0.56	0.15	0.11	0.27	−0.02	−0.16	0.18	−0.20	0.21	−0.04	−0.22	−0.09	0.05	0.13	−0.01	0.02	0.07	−0.10	1

Negative correlation ($r < -0.5$); Deep pink and positive correlation ($r > 0.5$); cyan colour.

Appendix 3. Types of Pesticides used in the Kahe catchment in Lower plain Moshi.

INSECTICIDES			
S/No	**Trade Name**	**Common Name**	**Target**
01	Dasba 40EC	Chloropyrifos	For against tomatoes
02	Duduba 450EC	Cypermethrin10%+ Chlorpyrifos 35%	Control of insect pests in roses
03	Dkdime	Dimethoate	Insect pests in tomatoes and roses
04	Ninja Plus 5EC	Lambda−cyhalothrin	Insect pests in roses and tomatoes
06	Tarantula 1.8 EC	Abamectin	Control of maize stalk Borers
07	Marshal 250 EC	Carbosulfan	Roses against aphids and mites
08	Profecron 720 EC	Profenofos	Control of diamondback moth in cabbages
09	Sapa Cypermethrin 2.5%ULV	Cypermethrin	Coffee, tobacco, rice, Sugarcane against chewing and sucking pests.
10	Thiodan 35 EC	Endosulfan	Various crops against Chewing and sucking Pests.
11	Avaunt 150SC (Du−Pont)	Indoxacarb	On cotton, brassicae, tomatoes, beans and vegetables against catepillars.
12	Dudu−Acelamectin 5% EC	Abamectin 2%+ Acetamiprid 3% and inert 95%	Various crops against Insect pests.
13	Dudumectin	Emamectin 4.8%+ Acetameprid 6.4%	
14	AQUAWET 15 SL	Ethoxylate 15%	
15	Agro Cron 720EC	Profenofos 725	
16	Prosper 720EC	Profenofos 60% + Cypermethrin 12%	
17	Wiltigo Plus 50 EC	Emamectin Benzoate 5%	
HERBICIDES			

01	Atranex 50 SC	Atrazine	Weeds in sugarcane plantations
02	Boxyfan 240 EC	Oxyfluorfen	Weeds in sugarcane plantations
03	Parastar 200SL	Paraquat dichloride	In maize, coffee, tea, sisal, cotton,, bananas, sugarcane against common leaves and annual weeds
04	Dk Gly 480SL	Glyphosate	Pre-plant application for control of weeds in coffee, tea, cashew and cereals
05	Wildbees 720 SL	2,4 D Amine	Control of weeds in sugarcane plantations
06	Glypro 4l SL	Phosphonomethly Glycine 48%	
07	Oxyfen 24% EC	–––	
08	Super Round	–––	
		FUNGICIDES	
01	Ebony 72 WP	Mancozeb 64%+Metalaxyl 8% WP	Against late blight disease in potatoes, tomatoes and grapes.
02	Sapa Copper Oxychloride	Copper oxychloride	Control of late blight on tomatoes

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