EQA - International Journal of Environmental Quality
ISSN 2281-4485 - Vol. 40 (2020): 11-18
Journal homepage: https://eqa.unibo.it/

published by

Investigation of physico-chemical characteristics and heavy metals concentration implying to the effect of local geology on surface water quality of Werii catchment, Tigray, Ethiopia

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Article info
Received 3/3/2020; received in revised form 30/3/2020; accepted 28/4/2020.
DOI: 10.6092/issn.2281-4485/10602

Abstract
The paper assesses the water quality parameters of Werii catchment in Northern Ethiopia. 27 water samples were collected and analyzed for 17 physico-chemical parameters. The electrical conductivity ranges 128-627µS/cm, while turbidity: 20-36.23NTU; total dissolved solids: 140.5-389 mg/L, and total alkalinity: 105-510 mg/L. The proportion of the samples exceeding WHO guidelines for drinking purposes in increasing order are Cu (16%), Cr (40%), As (44%), Ni (54%), Pb (64%), Fe (76%), Co (80%) and Zn (100%). One-sample testing confirmed that all but Fe significantly exceed the WHO guidelines values. The result of both One-way ANOVA and Factor analyses revealed Cr, Zn, Cu and Turbidity are associated with Werii slates in the first of five factors. Fe, As, Ni and Co are associated with Tsedia Slate in the second factor. The rest factors indicated that EC, TS, TSS and Co are attributed to Aiba basalt, Adigrat sandstone, Werii Slates and Tsedia Slates respectively.

Keywords
heavy-metals, surface water quality, factor analysis, lithounits

Introduction

Rivers are vital component of the biosphere that contains <1% of the world's fresh water with their higher ecological and social significance, even if the world's population increases drastically, yet, the amount of water will remain the same (Bishnoi and Arora, 2007). Besides the shortage, drinking water may be contaminated by different contaminants which may be geogenic (natural) and anthropogenic in sources, and their amount becomes beyond the required level leading to various deleterious effects on aquatic organisms (Murhekar, 2011; Annalakshmi and Amsath, 2012). According to Ali et al. (2004), determining the water quality parameters provide the basis for judging the suitability of water for its designated uses and to improve existing conditions. But, the nature and extent of water pollution is characterized by several physical, chemical and biological parameters as well as heavy metals concentration. The solubility of geological materials and increased anthropogenic activities have contributed to decline in water quality (climate, precipitation, soil type, vegetation, groundwater and flow conditions (Chitmanat and Traichaiyaporn, 2010). Quality of water can be regarded as a network of variables such as pH, oxygen concentration, temperature, etc. and any changes in these physico-chemical variables and heavy metals concentration can affect aquatic biota in a variety of ways (Kolawole et al., 2011). hence it is very essential to test the quality of the water before it is used for drinking, domestic, agricultural and industrial purposes. The utility of river water for various purposes is governed by physico-chemical, biological parameters and heavy metal concentration of the water (Singh et

DOI: 10.6092/issn.2281-4485/10602

al., 2013). Heavy metals are dangerous because they are non-biodegradable, bio-available and toxic for different crops (Mahler, 2003). Some of these heavy metals are mercury, arsenic and chromium (Lucho-Constantino et al., 2005). These elements are usually found as natural components of earth's crust, as minerals, salts and other compounds that can be absorbed by plants and incorporated into the food chain (Rooney et al., 2006; Zhao et al., 2006). They cannot be easily degraded, destroyed naturally or organically since living beings do not have specific metabolic functions for them (Abollino et al., 2002). In Tigray region, few studies have been conducted on heavy metal contamination of drinking water so far such as Mebrahtu and Samuel, (2011). But in the study area, there was no study conducted yet in this regard. For this reason, due emphasis is given to determine the levels of selected physico-chemical parameters and to analysis heavy metals concentration compared with local geology.

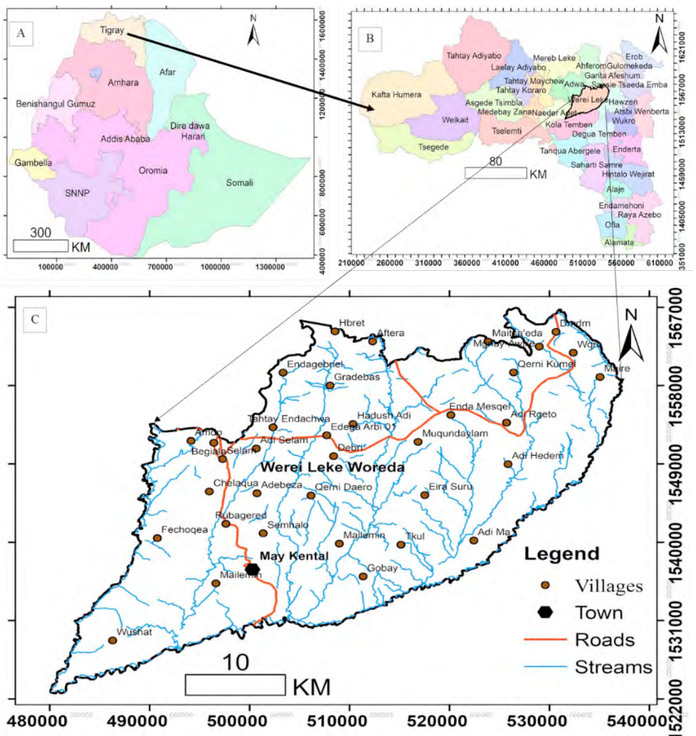

Figure 1. *Location map of the study area: A) Ethiopia, B) Tigray Region and C) Werii Basin.*

The Werii watershed is located in the Tekeze River basin, Northern Ethiopia (Fig. 1). Geographically, it extends from 13.843°–14.27°N latitude and 39.467°–39.016°E longitude. The topography of the watershed is characterized by undulating terrain with steep slopes, a fragile environment, erratic rainfall, and sparse vegetation coverage, which, in turn, leads to erosion. The elevation of the watershed ranges from 1363 to 3010 m.a.s.l and a semi-arid climate. The watershed receives about 77% of the annual rainfall in the summer (rainy) season (June, July, August, and September) and the remaining 23% in the winter (dry) season, from October to May. The dominant soil types of the watershed are silt clay loam, sandy loam, and silty loam, which comprise 49.5, 26.4, and 21.1% of the watershed area, respectively. Five land-use types are recognized, with crop land, shrub, forest, bare land, and grassland, covering 41.4, 28, 27, 2.7, and 0.5% of the watershed area, respectively.

The geology of the Werii watershed is constituted by the rocks ranging from Precambrian to the present (Fig. 2). 56.34 % of the total area of the basin is covered by the basement rocks and their associated intrusives. The Paleozoic, Mesozoic and Cenozoic rocks cover 16.91 %, 12.53 % and 14.22 % of the total area of the basin, respectively. The Tembien Group and the Didikama Formation are Metasediments, in contrast to the Tsaliet Group which is mainly of metavolcanics ranging in composition from basalts to dacites and rhyolites and associated Metasediments. The Metasediments include breccias, agglomerates, bedded tuffs and lavas, all interbedded with marine clastics, rare limestones, tuffaceous slates, redeposited ash and greywacke composed partly of volcanic fragments. The Tembien Group includes Werii Slate, Limestone and Ts'ediya Slate. The Didikama Formation consists of creamish to white dolomite alternating with gray, black or variegated slates. Syntectonic granites are light gray to pink, weakly to strongly deformed or recrystallized, medium grained and generally equigranular. These granites contain biotite, locally with muscovite and rarely with minor hornblende. The intrusions are black andesine dolerite with ophitic texture. The Enticho Sandstone and Edaga Arbi Glacial are resting unconformably on the Precambrian and form small conical hills or irregular slopes below the cliff of Adigrat Formation. The Aiba Basalts are Tertiary volcanic rocks, typical transitional basalts, very homogeneous in composition. They show a distinctive tholeiitic nature with transitions to mildly alkaline varieties. The Adwa Formation is composed of alkaline trachytic and phonolitic composition. The alkaline plugs form a youthful and peaked topography with flow structure, columnar jointing, concentric exfoliation and commonly form mountains of bare rock (Nata, 2003).

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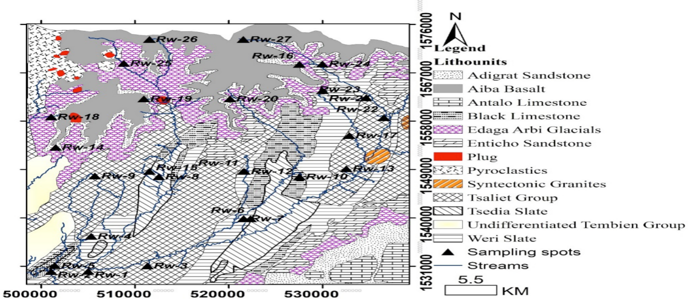

Figure 2. *Geological map with sampling sites in the study area (Modified after Nata, 2003).*

Materials and Methods

Twenty-seven River water samples from Werii River were collected for this study following standard procedure as described by APHA (1998) (Fig. 2). Pre-washed 500 mL sizes of PVC plastic bottles were used to collect water sample for water quality analysis. Sample containers were labeled on the field and temporary put in ice packed cooler and transported to the laboratory and stored in a refrigerator at about 4°C prior to analysis (Gangwar et al., 2012). Physico-chemical parameters: temperature, conductivity, total dissolved solids and salinity of the samples were measured on spot using Jenway 4150, portable conductivity meter as well as pH using Hach, HQ11d Portable pH Meter. In addition, Turbidity of the samples was measured at aquatic chemistry laboratory of Aksum University using Hach, 2100Q Turbidimeter. Similarly, heavy metals (As, Cd, Co, Cu, Cr, Fe, Ni, Pb and Zn) analysis was done at analytical laboratory of Ezana Mining Development P.L.C. using AA240FC, Varian instruments, Fast Sequential AAS Australia with instrument working condition mentioned. Analytical grade chemicals (HNO_3, Sigma chemicals, Australia and standard heavy metal solutions, Varian instruments, Australia) after preserving at 4°C for short period of time. All chemicals used were of analytical grade and the distilled water used is ultrapure deionized water. The same distilled water was used for the preparation of standards, and modifier solutions that were used for calibration by preparing standard solutions. Repeat analyses on four randomly selected samples were performed and reagent blanks and standards were used to assure quality control of analysis giving <10% precision and bias. The chemical used in the treatment plant was alum and lime for treatment of raw water and chlorine gas.

Data analysis

Both physicochemical parameters and heavy metals were analyzed through SPSS version 26.0, Microsoft Excel and spatial analysis was conducted using Arc GIS. One-way ANOVA, Factor analysis and one-sample testing were conducted to investigate the principal association of local geology with the parameters and the significance of the deviation from WHO guideline values respectively. In order to understand the possible effect of the local geology on the physicochemical characteristics of the stream water, spatial and statistical comparisons were conducted. In factor analysis, Principal Component Analysis and Varimax with Kaiser Normalization were used where Rotation converged in 7 iterations producing five factors.

Results and discussion

Physico-chemical characterization

The physico-chemical analytical result is presented in Table 1. EC is a measure of the dissolved ionic component in water and hence electrical characteristic that gives an indication of the amount of total dissolved substitution in water (Yilmaz and Cengiz, 2014). Values hhigher than the prescribed limit set by WHO for drinking purposes indicate the presence of high amount of dissolved inorganic substances in their ionized form (Sankpal and Naikwade, 2012). Higher the EC implies less amount of water will be available to the plants, drinking purpose and presence of more soluble geologic materials and mineral types.

The pH values ranging from 7.45 to 8.4 but within the permissible limit of WHO set for drinking (WHO, 2011; Ayers and Westcot, 1994). Turbidity, measure of transparency of water, values of the area ranges from 20-36.23 NTU. Higher values can be due to daily disturbance of the water by Artisanal gold miners and surface runoff. Turbidity values are higher than WHO, 5 NTU, for drinking purposes (WHO, 2011). The temperature of Werii catchment is likely suitable for aquatic lives. The measured total Alkalinity values ranges from 105-501 mg/L which are above the prescribed limit set by WHO (2011). These higher results may be due to weathering of geological materials, the presence of soluble mineral particles and waste discharge. Total Solids (TS) results ranges from 678 mg/l at GW-25 to 1932 mg/l at GW-18. This might be due to dissolution of geologic materials and deposition of domestic wastes from the surrounding. The value of TS concentration

DOI: 10.6092/issn.2281-4485/10602

is higher near to the urban areas compared to the rural areas. Similar findings are also reported by Varunprasath and Daniel (2010) with TS values 1030-1130 mg/L and 1630-1800 mg/L respectively. Total suspended solid content of water depends on the amount of suspended particle, soil and silt which is directly related to turbidity of water. The analyzed result of the present study ranges from 137 to 369; these values are attributed to the surface runoff and disposals of domestic sewage. Water having TSS values greater than 100 mg/L but less than 220 mg/L is classified as medium wastewater (Akan et al., 2008). One-sample testing confirmed that EC, TDS and Turbidity significantly (2-tailed) exceed the WHO guidelines values.

	pH	TS (mg/L)	TSS (mg/L)	Alkalinity (mg/l)	EC (µS/cm)	TDS (mg/L)	Temp. °C	Turbidity (NTU)
Minimum	7.45	678.00	137.00	105.00	128.00	166.50	21.60	20.00
Maximum	8.40	1932.00	369.00	510.00	778.00	1100.50	24.90	36.23
Mean	7.88	1335.77	240.26	267.04	447.81	478.76	23.42	27.84
Stdev	0.23	415.12	73.77	99.25	139.56	302.49	0.91	6.18
WHO, 2011	NGL*	-	-	-	250.00	500.00		5.00

Stdev= Standard deviation NGL*= No Guideline

Table 1. *The summary of analytical results of some physicochemical parameters of the study area.*

According to WHO (2011), the TDS level of drinking water must to be < 500 mg/L. Similarly, of the samples analyzed 66% were found to contain TDS values below the maximum permissible limits of WHO for the drinking purpose. But 44% of the drinking water samples exceed the maximum permissible limits of WHO for the drinking purpose. Drinking water becomes significantly and increasingly unpalatable at TDS Levels less than about 1000 mg/L and TDS greater than 1200 mg/L may be objectionable to consumers and could have impacts for those who need to limit their daily salt intake (London, 2005).

Heavy metals concentration status

The analytical result of heavy metals is presented in Table 2. Zn ranges from 785µg/L to 5320µg/L. Nevertheless, higher concentrations of Zn are unsuitable as the Zn salts cause an unpleasant taste, opalescence in alkaline waters and causes poisoning in human (Dkhar et al., 2014). All the mean value analyzed heavy metals exceeds the WHO maximum admissible limit of drinking water except Cu which ranged from 515 to 3515µg/L. The source of Cu may be from sulfides and artisanal gold mining activities in the sampling areas. Pb ranges from 8 to 1100 µg/L and occurs geologically in association with sulphide minerals, ores and coal (Reiman and Caritat, 1998). Ni concentrations range from 17 to 455 µg/L the primary source being leaching from metals in rocks. Chromium in drinking water is very low ranging from 10 to 50 µg/L except for the regions with substantial chromium deposits (Jayana, 2009). In this study area, Cr level varies from 15 to 150 µg/L. Arsenic level varies from 1.5 to 65 µg/L while Cadmium ranges from 1.25 to 11 µg/L. This can be attributed to runoff from the agricultural areas. One-sample testing confirmed that Cu, Zn, Pb, Cr, Ni, As and Cd significantly (2-tailed) exceed the WHO guideline values.

	Cu	Zn	Pb	Cr	Fe	Ni	As	Co	Cd
Minimum	515	785	8.00	15.0	110	12.9	1.50	89.0	1.25
Maximum	3515	5320	1100	150	1300	455	65.0	1500	11.0
Mean	1378	2102	396	55.0	726	128	19.8	564	3.94
Stdev	849	1527	425	34.4	404	143	19.5	427	2.29
WHO, 2011	2000	200	10.0	50.0	300	70.0	10.0	-	3.00
% age above limit	16	100	64	40	76	54	44	80	40

Table 2. *The summary of analytical results of heavy metals (in µg/l).*

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Effect of local geology

The Factor analysis produced five factors with total variance of 76%. The first factor contains Zn, Cr, Cu and Turbidity. One-way Anova associate these parameters with Werii slate rock unit. One can also observe their spatial distribution on the Spatial post plots in Figures 3, 4 and 5. Robust Tests of Equality of Means show that Zn and Turbidity in Werii Slate are significantly different from Adigrat Sandstone, Edaga-Arbi Glacial and Aiba Basalt while Cr and Cu are not. The second factor has As, Ni, Cd and TDS while the association showed that Tsedia Slates contributes more As and Ni; Aiba basalt attributed to Cd and Werii Slate loads more TDS. This can be likened with the spatial post plots in Figures 6-8 that show comparable spatial variability. However, only As in Tsedia Slate turned to be significantly different from Tsaliet group, Edaga Arbi Glacial and Aiba Basalt whereas the rest parameters in this factor exhibit homogeneity in the Litho-Units. The remaining factors contain poorly related parameters being predominantly loaded by different litho-units. Accordingly, EC, TS, TSS and Co are attributed to Aiba basalt, Adigrat sandstone, Werii Slates and Tsedia Slates respectively. Edga-arbi Glacial is presumed to contribute more Pb and Alkalinity. These parameters are not significantly different among the rock types according to one-way Anova and spatial post plots.

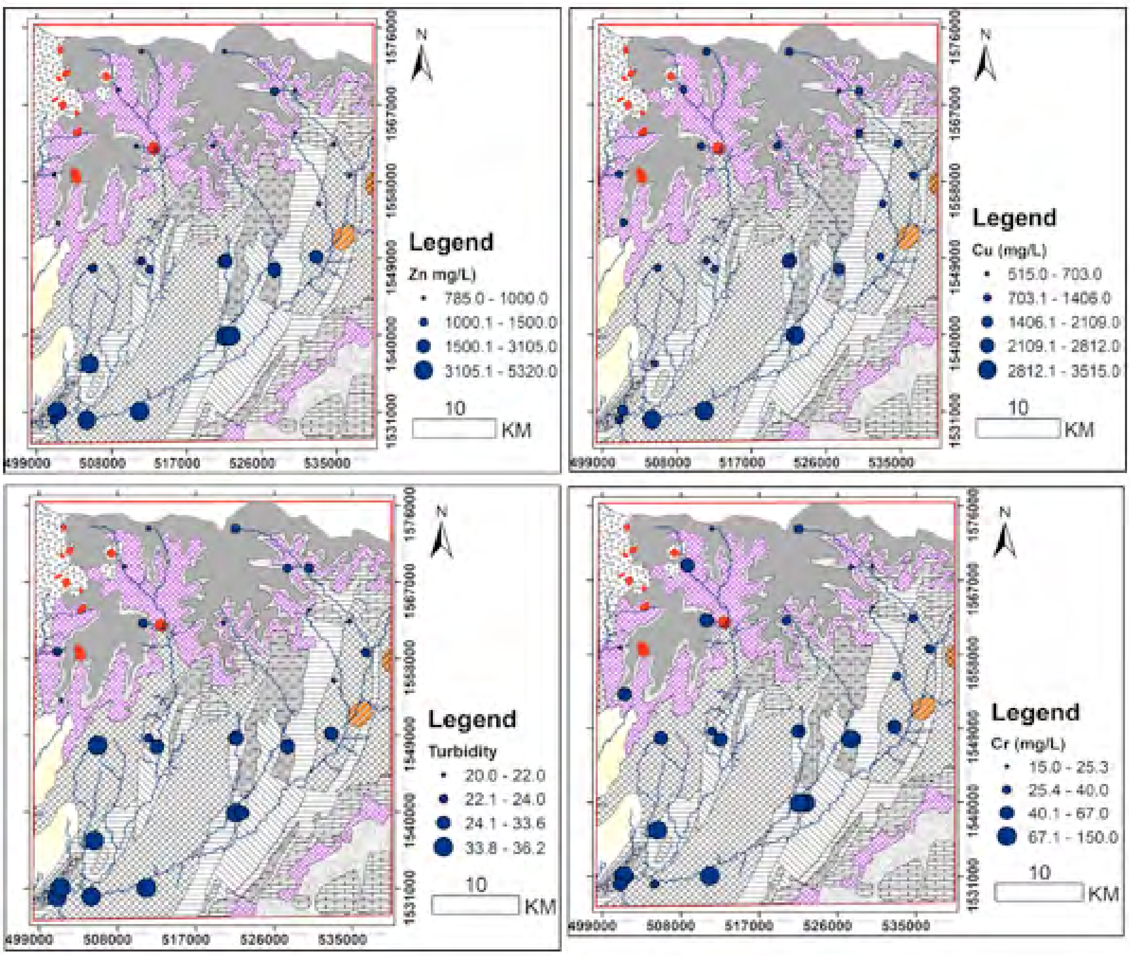

Figure 3. *Spatial post plots of parameters in the first factor with geological map.*

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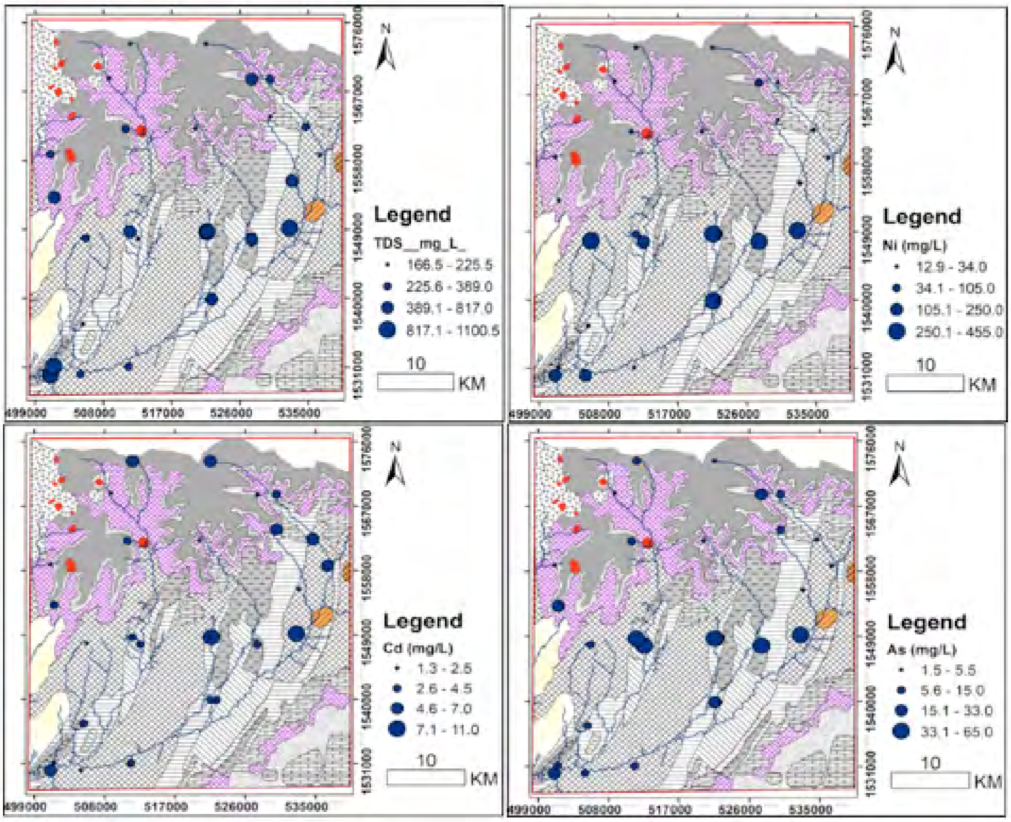

Figure 4. *Spatial post plots of parameters in the second factor with geological map.*

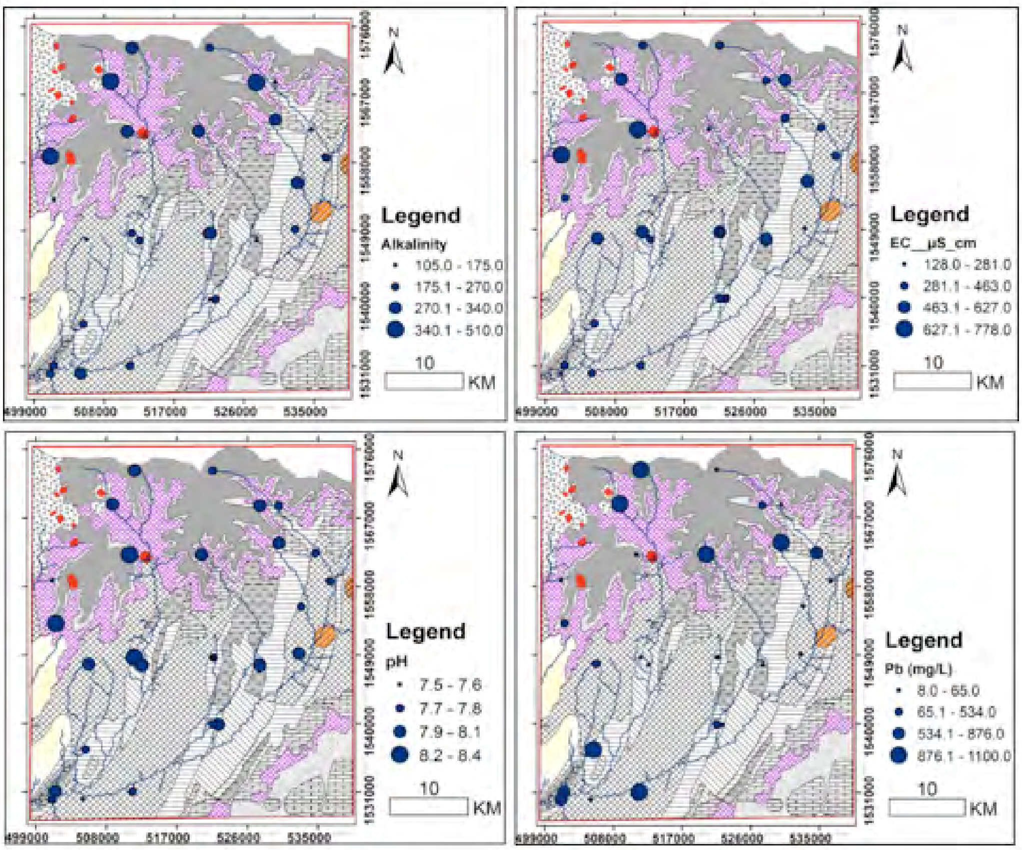

Figure 5. *Spatial post plots of parameters in the third factors with geological map.*

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Conclusions

Present investigation concludes that most of the studied physicochemical parameters and selected heavy metals concentration of Werii River water were found to be above the recommended limit of standards for drinking purpose. 8 physico-chemical water quality parameters and 8 heavy metals concentration obtained in the study were above the permissible limits of WHO (2011) standards for drinking water. The higher values of both the physico-chemical water quality parameters and heavy metals concentration of certain contaminants also indicate that the Werii River water will be unsafe for domestic purposes without some forms of physical and chemical treatments. The analyzed water samples showed that there are significant differences among the different sampling sites which might be due to the different factors (natural and anthropogenic activities). This might be due to both natural processes and anthropogenic activities, then the water is not potable for domestic purposes without some forms of physical and chemical treatment while it is useful for agricultural purposes. Factor analysis and one-way Anova indicates that the local geology has significant role in governing the physicochemical characteristics and heavy metal loadings. Spatial variability patterns strengthen this observation. It is recommended that effective management of the Werii River is required in order to minimize some problems associated to human health. There is also an urgent need for public awareness on the state of the water and apply legal and relevant laws regarding proper treatment of industrial and domestic discharge before entering to the river course.

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