

Assessment of the Effect of Tulu Kapi Gold Mining Project Related Wastes on the Status of Physico-Chemical Parameters of Gomo and Guracho Streams Water

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Abstract: The study was conducted to assess the effect of Tulu kapi gold mining related wastes on Guracho and Gomo streams water by analysis of physico-chemical parameters of the water samples. Guracho and Gomo streams are located in, Genji District, West Wollega Zone, Oromia, Ethiopia. Water samples were collected during rainy and dry seasons from five sites of Guracho and Gomo streams. The amounts of Cr, Cu, Fe, Mn, NO₃⁻, PO₄³⁻, SO₄²⁻, total hardness, total chlorine and dissolved oxygen were determined using HACH DR/2400 portable spectrophotometer. Zinc concentration was analyzed using atomic absorption spectroscopy. Chemical oxygen demand and chloride concentration were analyzed using open reflux and titration methods respectively. Turbidity was determined by turbidity meter. Temperature and pH was measured using pH/temperature meter while total dissolved solid and electrical conductivity were measured using TDS/conductivity meter. Relative to the WHO guide line, the streams water samples were found to have higher turbidity ranged from 5.68 to 14.29 NTU, higher Fe concentration at Guracho upstream (0.55 mg/L), Gurachodownstream (0.47mg/L) and Gomo upstream (0.53 mg/L). The ranges of mean values of obtained results for other parameters were; pH 6.47 - 6.85, electrical conductivity 40.71 - 104.61 μS/cm, total dissolved solids 19.61- 40.37 mg/L, total suspended solids 0.02 - 0.06 mg/L, total hardness 2.99 - 3.34 mg/L Ca and Mg as CaCO₃. The concentration of other chemical parameters in mg/L were: SO₄²⁻ 2.92 - 4.42, NO₃⁻ 2.45 - 4.15, PO₄³⁻ 0.19 - 0.65, Cl⁻ 25.03 - 45.05, Chlorine total 0.05 - 0.11, dissolved oxygen 7.36 - 11.33, Cr 0.02 - 0.14, Cu 0.01 - 0.26, Mn 0.03- 0.63 and Zn 0.09- 0.63. These parameters were generally acceptable according to WHO recommended values for both drinking and agricultural purposes.

Key words: Acid Mine Drainage • Heavy Metals • Gomo-Guracho Streams • Spectrophotometer

INTRODUCTION

Water pollution is a major global problem which requires ongoing evaluation and revision of water resource policy at all levels. The health of community highly depends on the availability of safe and adequate water for drinking, domestic use and personal hygiene. Diseases related to contamination of drinking-water constitute a major burden on human health and it has been suggested that water pollution is the leading worldwide cause of deaths and diseases [1, 2]. It has also

been known that inadequate water supply both in terms of quantity and quality coupled with poor sanitation globally account for approximately 30, 000 deaths daily. Many of them are infants and 80% of such cases occur in rural areas. The lack of suitable waste treatment results in discharges of untreated or inadequately treated sewage into aquatic environments, leading to deleterious health effects. Water courses that receive sewage also become sinks for anions such as Cl⁻, SO₄²⁻, NO₃⁻. The inorganic chemicals hold a greater portion as contaminants in drinking water in comparison to organic chemicals [3-5].

The causes of water pollutions are specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens and physical changes such as elevated temperature and discoloration. While many of the chemicals and substances that are regulated may be naturally occurring metals such as copper (Cu), Zinc (Zn), chromium (Cr), iron (Fe) and manganese (Mn) ions. The presence of heavy metals in stream water may also be harmful to human population through chronic poisoning [1]. Their concentration is often the key in determining the level of water contaminants. High concentrations of naturally occurring substances can have negative impacts on aquatic flora and fauna. The chemical constituents of irrigation water can affect plant growth directly through toxicity or deficiency, or indirectly by altering availability of nutrients [6]. Elevated concentrations of heavy metals in the soils and streams, accompanied with acidic pH, are likely to enhance up take of heavy metals by plants and man, which poses a high health risk to the people who consumes the contaminated agricultural products [7]. Oxygen-depleting substances may be natural materials such as plant matter as well as other man-made chemicals. Other natural and anthropogenic substances may cause turbidity (cloudiness) which blocks light and disrupts plant growth and clogs the gills of some fish species [8]. High turbidity in mining areas is an indication of land disturbances and can also decrease drinking water disinfection efficacy [9]. Particularly in rural areas, high turbidity may lead to higher rates of gastrointestinal diseases since many people consume unfiltered or untreated surface and ground water. Many of the chemical substances such as excess chloride, nitrate cyanides and sulphates are toxic [10, 11].

Mining causes water pollution through the exposure and oxidation of mineralized rock. Open-pit mining involves the excavation of large quantities of waste rock, material not containing the target mineral, in order to extract the desired mineral ore. The types of mine waste problems are numerous, but the most difficult one to address is the acid mine drainage (AMD) that emanates from both surface and underground workings [12]. Surface impacts of AMD are mostly from tailings and rock dumps and adversely affect both groundwater and surface water quality [13]. According to [14], the releases of AMD causes low pH, high electrical conductivity, elevated concentrations of Fe, Zn, Cr and other toxic heavy metals. Because the acid produced dissolves salts and mobilizes heavy metals from mine workings.

Water contamination caused by AMD is a significant environmental problem in some parts of the world, particularly in densely populated developing countries where human habitats are usually in close proximity to mine sites [15]. There is gold mining company at Tulu Kapi which is located in West Wollega Zone, Genji District, where the local residents have close proximity to the mining site. The source of Gomo and Guracho streams are found closer to the mining station. The local community around Tulu Kapi uses water from Gomo and Guracho streams for drinking and irrigation purposes. The quality of the streams water need to be assessed continuously because a number of chemical contaminants generate from mining area may affect aesthetic quality of the water. It can also cause adverse health effects on the local community as consequence of prolonged exposure through drinking-water [16]. Therefore, present study was initiated to investigate the effect of Tulu Kapi gold mining related wastes on the status of physico-chemical quality parameters of Gomo and Guracho streams water.

MATERIALS AND METHODS

Descriptions of the Study Area: The study area, Tulu Kapi, is located 441 km from Addis Ababa, in Western Oromia, Ethiopia and between altitude of 1, 600 m and 1, 765 masl. It is in West Wollega Zone, Genji District, which is 46 km from Gimbi town to the West and 13 km from Genji town to the West. Genji District has temperate climate with annual temperature varies between 18 to 32°C having rainy season and dry season (data obtained from Genji District Agricultural office). The location map of the study area was shown below in Fig. 1

Site Selection and Sampling Methods: There were five sampling sites selected (1A, 1B, 2A, 2B and C). Site 1A was from Guracho-stream which was very close to the mining area. The other was site 1B from Guracho stream which was 200 m down from site 1A. Site 2A was from Gomo, stream which was also very close to the mining area. Another was site 2B, 200 m down from site 1B. Site C was 200 m down the stream from site 1B and Site 2B. From all selected sampling sites, the water samples were collected from three points which were 10 meters apart by composite sampling method. The sampling frequency was twice during rainy season (June -August) and once in dry season (October), 2016.

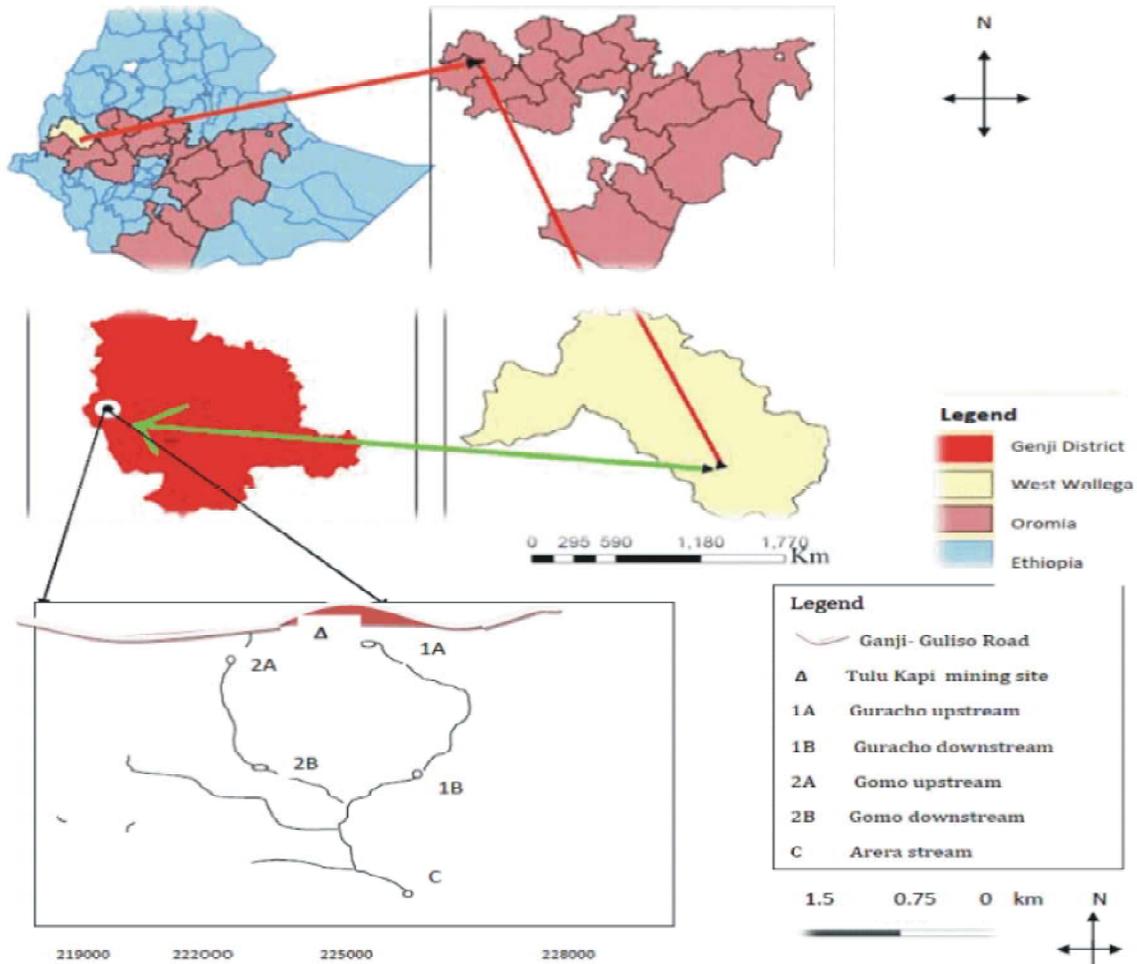


Fig. 1: Location map of the study area (Source: Arc view software)

Sample Preservation: ALL polyethylene bottles were thoroughly cleaned by rinsing with distilled water before adding the samples. For NO_3^- determinations, the plastic bottles were soaked in diluted HCl and then rinsed with deionized water. For Cl^- and PO_4^{3-} determination, the plastic bottles were soaked in HNO_3 and then rinsed with deionized water. The samples were transported to the laboratories using icebox and analyzed within specific times as described in literature review [17].

Experimental Analysis of Thewater Samples: All chemicals and reagents used in the present experimental procedures were obtained from Wollega University, East Wollega Zone Water supply laboratory (Nekemte), Ambo University and Addis Ababa University.

Instrumentation and Apparatus: The water quality parameters: Cr, Cu, Fe, Mn, NO_3^- , PO_4^{3-} , SO_4^{2-} , total hardness (TH), total chlorine and dissolved oxygen (DO)

were determined using HACH DR/2400 portable spectrophotometer, HACH Company, U.S.A. Zn concentration was analyzed using high performance AAS incorporating a graphite furnace for electro thermal atomization, PerkinElmer instrument, Shalto, CT 06484 USA, An ISO 9001 Company. Temperature of the water samples were measured using pH/temperature meter of model Z-WAG-WE 30020, Singapore. The pH of the water samples were also measured using pH /temperature meter of model Z-WAG-WE 30020, Singapore. Electrical conductivity and total dissolved solids were measured using Conductivity/TDS meter of model WGEC TEST 11PLS, Singapore. Turbidity was measured using turbidity meter model WZS-200, China. Evaporation and filtration apparatus as well as electronic balance of model ESJ 200-4 were used to determine total dissolved solids (TDS) and total suspended solids (TSS). Argentometric titration method was used to determine chloride ion concentration.

Table 1: Method Performance and Sensitivity of the instrument (HACH DR/2400)

Parameters	Precision		Sensitivity
	Standard concentration (mg/L)	95% Confidence limits of distribution (mg/L)	Δ Con (mg/L) for each Δ abso of 0.010 (MDL)
Hardness	2.50 Ca as CaCO ₃	2.36–2.64 Ca as CaCO ₃	0.05 Ca
	2.16 Mg as CaCO ₃	2.08–2.24 Mg as CaCO ₃	0.02 Mg
Cr	0.25 Cr	0.24–0.26 Cr	0.01 Cr
Mn	0.500 Mn	0.492–0.508 Mn	0.01 Mn
Cu	1.000 Cu	0.96–1.04 Cu	0.04 Cu
Fe	1.000 Fe	0.990–1.010 Fe	0.02–3.0 Fe
DO	36.0 O ₂	33.3–38.7 O ₂	0.34 O ₂
NO ₃ -N	10 NO ₃ -N	8.0–12.0 NO ₃ -N	0.30 NO ₃ -N
PO ₄ ³⁻	1.00 PO ₄ ³⁻	0.97–1.03 PO ₄ ³⁻	0.02 PO ₄ ³⁻
SO ₄ ²⁻	30 SO ₄ ²⁻	27–33 SO ₄ ²⁻	1.0 SO ₄ ²⁻
Cl ₂	1.07 Cl ₂	1.05–1.09 Cl ₂	0.02 Cl ₂

MDL –Method Detection Limit, Δ abs- change in absorbance, Δ con- change in concentration, DO- Dissolved Oxygen, Cl₂- Total chlorine

Estimating Precision: The concentration change equivalent to an absorbance change of 0.010 was the estimated lower detection limit of each test for Hach DR/2400. The standards were analyzed seven individual times on a single instrument with the two reagent lots of originally used in the calibration. A standard deviation of each of the two sets of seven values was calculated and 95% confidence interval of the distribution was reported.

Method detection limit (MDL) was calculated from the student replicate study result multiplied by the appropriate student's t-value for 99% confidence interval (Table 1).

$$MDL = \text{student } t \times S \tag{1}$$

Statistical Data Analysis: The obtained data of water samples were treated using SPSS software program. Descriptive statistical analysis and one-way analysis of variance (ANOVA) were applied to assess variations among sites and their Pearson's simple correlation coefficients.

Analysis of Selected Physical Parameters of the Water Samples

Temperature (?): Temperature measurement was made by using pH/temperature meter at sampling site. It was done by taking a portion of the water sample and immersing the probe into it for a sufficient period of time (till the reading stabilizes).

Turbidity: Turbidity meter was calibrated using distilled water and a standard turbidity suspension (formazine suspension). The samples were shaken thoroughly and measured in the nephelometric turbidity meter [8].

Total Dissolved Solids (TDS): The TDS was measured using Conductivity/TDS meter. The other method was by using filtration and evaporation method by first determining total solid as follows.

$$\text{Total Solids (mg/L)} = \frac{(W_1 - W_2)(1000)}{\text{Sample volume (ML)}} \tag{2}$$

where: W₁ = Weight of dried residue + dish, W₂ = Weight of empty dish

The difference in the weights of Total Solids (W₁) and Total Suspended Solids (W₂) expressed in the same units gives Total Dissolved Solids (TDS), which can be calculated as follows.

$$TDS \text{ (mg/L)} = \frac{(W_1 - W_2)(1000)}{\text{Sample volume (ML)}} \tag{3}$$

where : W₁ = Weight of total solids + dish, W₂ = Weight of total suspended solids [17].

Total Suspended Solids (TSS): TSS is the portion of solid that is retained on the filter of standard specified size under specific conditions. A well – mixed sample was filtered through a weighed standard glass fiber filter and the residue that was retained on the filter was dried to a constant weight at a temperature of 103-105 ?. The increase in the weight of the filter determines the TSS. The values were calculated using the following equation.

$$TSS \text{ (mg/L)} = \frac{(W_1 - W_2)(1000)}{\text{Sample volume (ML)}} \tag{4}$$

where: W₁ = Weight of dried glass fiber filter + residue and W₂ = Weight of glass fiber filter disk before filtering [17].

pH of the Water Samples: The pH was measured at the sampling sites using portable pH/Temperature meter which was calibrated with three standard solutions (pH 4.0, 7.0 and 10.0), before taking the measurements.

Electrical Conductivity (EC): The EC of the water samples was measured using TDS/conductivity meter in micro Siemens per cm ($\mu\text{s}/\text{cm}$). The probe was calibrated using a standard solution with a known conductivity value.

Analysis of Selected Chemical Parameters of the Water Sample

Total Hardness (TH): The TH was determined by calmagite colorimetric method using Spectrophotometer at 522 nm. The indicator dye was calmagite, which forms a purplish-blue color in a strongly alkaline solution and changes to red when it reacts with free Ca or Mg. The Ca and Mg determinations were made by chelating Ca with EGTA to destroy any red due to Ca and then chelating the Ca and Mg with EDTA to destroy the red color due to both Ca and Mg. By measuring the red color in the different states, Ca and Mg concentrations were determined as Ca and Mg hardness respectively. The sum of both Ca & Mg hardness gives total hardness [18].

Nitrates (NO_3^-): The NO_3^- concentration was determined by Cd-reduction method using Spectrophotometer at 500 nm. The Cd metal reduces nitrates in the sample to nitrite. The NO_3^- reacts in an acidic medium with sulfanilic acid to form an intermediate diazonium salt. The salt couple with gentisic acid to form amber colored solution [19].

Total Phosphate (PO_4^{3-}): The total PO_4^{3-} was determined by Phos Ver 3 (Ascorbic Acid) method using Spectrophotometer at 880 nm. Orthophosphate reacts with molybdate in an acid medium to produce a mixed phosphate molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue color [20].

Sulphates (SO_4^{2-}): The SO_4^{2-} concentration was determined by SulfaVer4 Method using Spectrophotometer at 450 nm. SO_4^{2-} in the sample reacts with barium in the SulfaVer4 and form a precipitate of barium [21].

Chlorides (Cl): The Cl⁻ was determined by Mohr's method of argentometric titration [22, 23]. In alkaline or

neutral solution, potassium chromate indicated the endpoint of the silver nitrate titration of chlorides. Silver chloride was quantitatively precipitated before the red silver chromate was formed. The result was calculated as follows.

$$\text{Cl}^- (\text{mg/L}) = \frac{(A - B)(N)(35.45)}{\text{Sample taken in ML}} \quad (5)$$

where: A - Volume of silver nitrate consumed by the sample, B - Volume of silver nitrate consumed by the blank and N - Normality of silver nitrate [23].

Total Chlorine: Total Chlorine was determined by DPD method using spectrophotometer at 530 nm. Chlorine can be present in water as free chlorine and as combined chlorine. Both forms can exist in the same water and be determined together as the total chlorine. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine and free chlorine reacts with DPD (N, N-diethyl-p-phenylenediamine) to form a red color which is proportional to the total chlorine concentration [24].

Dissolved Oxygen (DO): The DO was determined by Ultra High Range Method using Spectrophotometer at 680 nm. The High Range of DO AccuVac Ampule contains reagent vacuum sealed in a 12-mL ampule. When the AccuVac Ampule was broken open in a sample containing dissolved oxygen, a yellow color was formed which turns purple. The purple color development is proportional to the concentration of dissolved oxygen [25].

Chemical Oxygen Demand (COD): The COD is the measure of oxygen equivalent to the organic content of the sample that is susceptible to oxidation by a strong chemical oxidant. It was measured by the open reflux method using COD digester [22]. The result was then calculated as follows.

$$\text{COD}(\text{mg/L}) = \frac{(\text{Blank reading} - \text{Sample reading}) (N)(F)(100)}{\text{Sample taken in ML}} \quad (6)$$

$$\text{To calculate F, } F = \frac{10000}{\text{Titrant value of the blank}} \quad (7)$$

where: COD = chemical oxygen demand, F= decimal volumetric factor and N = normal concentration of the titrant.

Analysis of Selected Heavy Metals (Cr, Cu, Fe, Mn and Zn) in the Water Samples:

Chromium (Cr): The Cr was determined by the 1, 5-Diphenylcarbohydrazide method using a single dry powder formulation called Chroma Ver 3 Chromium Reagent by Spectrophotometer at 540 nm. This reagent contains an acidic buffer combined with 1, 5-Diphenylcarbohydrazide, which reacts to give a purple color when hexavalent chromium is present [26].

Copper (Cu): The concentration of Cu was determined by bicinchoninate method using Spectrophotometer at 560 nm. The Cu in the sample reacts with a salt of bicinchoninic acid contained in CuVer 1 or CuVer 2 Copper reagent to form a purple colored complex in proportion to the Cu concentration [27].

Iron (Fe): The concentration of Fe was determined by FerroVer method using Spectrophotometer at 510 nm. FerroVer Iron Reagent converts all soluble iron and most insoluble forms of iron in the sample to soluble ferrous iron. The ferrous iron reacts with the 1, 10 phenanthroline indicator in the reagent to form an orange color in proportion to the Fe concentration [28].

Manganese (Mn): The concentration of Mn was determined by PAN Method using Spectrophotometer at 560 nm. An ascorbic acid reagent was used initially to reduce all oxidized forms of Mn to Mn^{2+} . An alkaline-cyanide reagent was added to mask any potential interference. PAN Indicator was then added to combine with the Mn^{2+} to form an orange-colored complex [29].

Zinc (Zn): The Zn was analyzed by AAS using electro thermal atomic absorption method at wave length of 213.86 in an estimated detection limit of $2\mu g/L$. The alternative wave length was 206.20 nm when the calibration is $5.0\mu g/L$ concentrations and its upper limit concentration was $100\mu g/L$. To prepare Standard Zn solution, 1.000 g of zinc metal was dissolved in 20 ML of Hcl and diluted to 1000 ML in distilled water, to give $1ML = 1\text{ mg}$ of Zn. A series of standards ranging from 1mg to 5 mg were prepared from the stock and analyzed using the methods in the literature [30].

RESULTS AND DISCUSSION

Physical Parameters of the Water

Water Temperature: In the present study the temperature

of water samples ranged from 20.14 - 21.19 °C (Table 2), which has no effect on formation of undesirable change on physical and chemical properties of the streamswater.

Turbidity: The lowest water turbidity value 5.68 and highest 14.29 NTU were recorded from site 2B (Gomo downstream) and site 1B (Guracho downstream), respectively (Table 2). The higher turbidity value recorded might be due to the continuous gold searching activity around the streams. The results obtained from the present study indicated that turbidity values of all the water samples were above the maximum limit recommended by WHO and EGL for drinking water, which was 5 NTU. The one way ANOVA test ($p < 0.05$) revealed that there was positive correlation between turbidity and TDS values (Table 3 and 4). The average mean values of turbidity recorded in rainy and dry season were 10.41 and 9.49 NTU respectively.

Total Dissolved Solids (TDS): The minimum value of TDS (19.62) and the maximum value (40.38) mg/L were recorded at site C and site 1B respectively (Table 2). In rainy season and dry season the total dissolved solids concentrations were 35.97 and 26.43 mg/L respectively (Table 3). This variation was due to the fact that waste assimilation capacity increases in the rainy season. TDS values showed positive correlation with turbidity, all analyzed heavy metals and EC (Table 4). This confirmed that increasing metal ions concentration increases the TDS as well as the EC of the water. Even though TDS is not considered as primary water pollutant, high level of TDS in water has aesthetic problems such as bitter and salty taste [31]. The WHO [1] standard limit for TDS in terms of drinking water was 1000 mg/L. According to [32] water with TDS $> 2000\text{ mg/L}$ causes clogging problem in localized irrigation system. So in this respect it can be concluded that the streams water is acceptable from the drinking water perspective and also for irrigation purpose.

Total Suspended Solids (TSS): The TSS values of all the streams water samples were very little. Their range was between 0.02 mg/L at site 1B and 0.06 mg/L at site 2B.

pH of the Water Samples: The mean pH values of water samples at sites 1A and 1B were 6.61 and 6.66 respectively, but for sites 2A and 2B were 6.49 and 6.85 respectively however, for site C it was 6.84. These results indicated that there were slightly increasing pH values down the streams as we go far from the mining area.

Table 2: Mean values (±SD) of physico-chemical parameters of Gomo and Guracho streams water with drinking water quality standard of WHO

Parameters	(Site 1A)	(Site 1B)	(Site 2A)	(Site 2B)	(Site C)	[1]
Temp.(°C)	20.14±0.39	21.19±1.29	21.02±1.12	20.63±0.19	20.72±0.46	-
PH	6.61±0.72	6.66±0.45	6.49±0.53	6.85±0.12	6.84±0.44	-
EC (µs/cm)*	104.60±290	81.58±12.18	48.04±2.57	40.72±2.77	55.77±1.39	<1500
Turb (NTU)*	11.08±0.75	14.29±1.73	9.71±1.84	5.68±0.82	8.98±0.47	< 5
TDS (mg/L)*	37.25±1.79	40.38±2.79	31.03±2.09	27.73±1.79	19.62±0.68	<1000
TSS (mg/L)*	0.03±0.01	0.02±0.01	0.05±0.02	0.06±0.01	0.05±0.01	-
TH (mg/L)	2.64±0.15	2.99±0.28	3.33±0.09	3.34±0.48	3.21±0.18	< 200
DO (mg/L) O ₂	7.36±1.33	8.08±1.9	8.24±0.35	9.14±1.44	11.33±1.10	-
COD (mg/L)*	6.40±0.05	1.60±0.00	8.80±0.01	8.80±0.04	9.6±0.03	-
SO ₄ ²⁻ (mg/L)	2.92±0.11	4.42±0.56	13.08±1.25	8.50±0.49	6.67±0.82	<250
NO ₃ ⁻ (mg/L)*	2.50±0.44	3.33±0.08	2.68±0.16	2.45±0.42	4.15±0.68	< 50
PO ₄ ³⁻ (mg/L)	0.65±0.05	0.63±0.05	0.19±0.03	0.23±0.15	0.49±0.09	-
Cl ⁻ (mg/L)	33.04±0.06	25.03±0.06	45.05±0.05	32.04±0.06	41.05±0.46	<250
Cl ₂ (mg/L)	0.09±0.01	0.10±0.01	0.07±0.01	0.04±0.02	0.02±0.01	-

Parameters indicated by* showed significantly difference among sites (p< 0.01).According to WHO [1] and EGL [34] , DO- Dissolved Oxygen, TH- Total Hardness (Ma and Ca as CaCO₃), Turb- Turbidity, Temp-Temperature, EC- Electrical Conductivity, TDS- Total Dissolved Solids, TSS- Total Suspended Solids, Cl₂-Total Chlorine, SD- standard deviation.

Table 3: Averages means of selected water quality parameters of Gomo and Guracho streams at each season

		Turb	SO ₄ ²⁻	NO ₃ ⁻	PO ₄ ³⁻	Fe	Cr	Cu	Mn	pH	EC	TDS
Rainy season	Mean	10.41	10.63	3.27	0.22	0.46	0.19	0.13	0.29	6.26	58.15	35.97
	Std.	2.23	3.67	0.33	0.09	0.09	0.01	0.06	0.08	0.32	8.03	9.95
	Mean	9.49	3.60	2.77	0.6	0.28	0.04	0.09	0.25	7.12	74.13	26.43
Dry Season	Std.	1.97	0.84	0.17	0.18	0.02	0.01	0.01	0.04	0.10	23.06	5.79

Turb - Turbidity, EC-Electrical conductivity, TDS-Total dissolved solids,

Table 4: Pearson's correlation analysis of quality parameters of Gomo and Guracho streams water

Par	Tur	DO	SO ₄ ²⁻	NO ₃ ⁻	PO ₄ ³⁻	Fe	Cr	Cu	Mn	Tem	PH	EC	TDS
Tur	1												
DO	-0.32	1											
SO ₄ ²⁻	-0.07	-0.52**	1										
NO ₃ ⁻	0.21	0.13	0.03	1									
PO ₄ ³⁻	0.18	0.46*	-0.51**	0.06	1								
Fe	0.43*	-0.59**	-0.07	-0.19	-0.39*	1							
Cr	-0.09	-0.67**	0.33	-0.42*	-0.39*	0.28	1						
Cu	0.69**	-0.35	-0.32	-0.03	-0.20	0.69**	0.01	1					
Mn	0.46*	-0.52**	-0.8	-0.31	0.31	0.49**	0.29	0.37*	1				
Tem.	0.33	-0.56**	0.65**	0.28	-0.59**	0.22	0.18	0.26	-0.09	1			
PH	-0.28	0.83**	-0.53**	-0.09	0.58**	-0.49**	-0.72**	-0.26	-0.20	-0.49**	1		
EC	0.39*	-0.04	-0.30	-0.05	0.83**	-0.08	-0.03	-0.04	0.66**	-0.31	0.20	1	
TDS	0.53**	-0.82**	0.04	-0.19	-0.28	0.76**	0.49**	0.72**	0.63**	0.42*	-0.59**	0.16	1

Significance level: **Correlation is significant at (p <0.01) (2-tailed); *Correlation is significant at (p<0.05) (2-tailed). Par- Parameters, Tur- Turbidity, DO- Dissolved Oxygen, Tem.-Temperature, EC- Electrical Conductivity, TDS- Total Dissolved Solids

Data obtained from the Pearson's correlation analysis indicated that pH values showed negative correlation with the heavy metals and SO₄²⁻ concentration (Table 4). This shows that the heavy metals in the water increase with increasing of metal sulphides that have capable of forming acidity and hence decrease the pH values. The average pH value of the rainy season and dry season were 6.26 and 7.15 respectively (Table 3). The normal

drinking water pH range mentioned in WHO and EGL guidelines was between 6.5 and 8.5 (Table 2). However, according to the WHO standard for drinking, water from Guracho and Gomo streams was not considered as acidic.

Electrical Conductivity (EC): According to WHO guidelines [1] conductivity of water for drinking and agricultural purpose was 1500 and 750 µS/cm respectively.

However water with conductivity value 750-2250 $\mu\text{S}/\text{cm}$ is widely used for agriculture [32]. In the present study the results obtained from the measured conductivity values of all water samples ranged from 40.72 $\mu\text{S}/\text{cm}$ at site 2B to 104.60 $\mu\text{S}/\text{cm}$ at site 1A. Conductivity decreased down the stream for all sites together with the decreasing value of TDS (Table 2). The reason for this difference might be because of higher mineral content of the stream water near to mining area. The other reason may be for increasing of water volume down the streams.

High conductivity may lead to lowering the aesthetic value of the water by giving mineral taste to the water [32]. Conductance values for the water samples obtained in dry season was 74.13 $\mu\text{S}/\text{cm}$ which was relatively higher than that of the values obtained in rainy season (58.15 $\mu\text{S}/\text{cm}$). In the dry season, the total volume of water decreases, as a result the conductivity increases.

Chemical Parameters of the Water

Chloride (Cl^-) and Total Chlorine: The lowest Cl^- concentration was 25.03 and the higher 45.05 mg/L at site 1B and 2A respectively. There was decreasing concentration of Cl^- down in both, Gomo and Guracho streams along with decreasing values of EC. This confirms that increasing Cl^- ion contributed to increasing of EC (Table 2). According to WHO standard limit for drinking purpose, Cl^- concentration in water was 250 mg/L. Irrigation water with concentration of chloride that exceed 900 mg/L is considered non-suitable for all agronomic [33]. Therefore for drinking and for irrigation purpose, the streams water was not polluted in term of Cl^- concentration. The total chlorine concentration of all sampling site ranged between 0.02 - 1.0 mg/L which was very less compared to 5 mg/L of the WHO [1] and EGL [34] drinking water standard limit of total chlorine concentration.

Phosphate (PO_4^{3-}): In the present study the PO_4^{3-} concentration of the streams water ranged from 0.19-0.65 mg/L in different seasons. The average PO_4^{3-} concentration of the streams water during rainy and dry seasons were 0.66 and 0.22 mg/L respectively (Table 3). The standard limit for PO_4^{3-} concentration was not set by WHO [1]. However, according to drinking water quality as per European Community, the maximum limit of PO_4^{3-} concentration for drinking water was 5.0 mg/L [35].

Nitrate (NO_3^-) and Sulphate (SO_4^{2-}): In the present study, the NO_3^- concentration fluctuated between 2.45-4.150 mg/L

at site 2B and C respectively. Relatively the highest concentration of NO_3^- was recorded at site C. However, according to the WHO guide line for drinking water the maximum concentration of NO_3^- was 50 mg/L. Results of the present study revealed that there was no pollution of the streams water regarding NO_3^- concentration. In the present study the SO_4^{2-} concentration ranges from 2.92-13.08 mg/L at site 1A and at site 2A respectively. In the rainy season the average SO_4^{2-} concentration was 10.63 mg/L and in dry season 3.60 mg/L. SO_4^{2-} ion concentration increases along with decreasing pH values upstream. Hence, there was negative correlation value ($p < 0.01$) between SO_4^{2-} ion concentration and pH value (Table 4). The WHO and EGL recommended value of SO_4^{2-} ion concentration for drinking water was less than 250 mg/L but less than 20 mg/L for agricultural purpose [35]. However, from the present study no pollution of the streams water in case of SO_4^{2-} ion concentration relative to the WHO and EGL water quality standard.

Dissolved Oxygen (DO) and Chemical Oxygen Demand

(COD): The DO values for Gomo and Guracho streams water lie in between 7.36 - 9.14 mg/L (Table 4). In the present study, DO increases down the streams and relatively higher dissolved oxygen mean value was observed at site C. This may be at site C, there were other two streams water which were added to it having their source not from the mining site (Fig. 1). DO values showed negative correlation values with turbidity, TDS, SO_4^{2-} , Fe, Cr, Mn and Cu. But positive correlation was values observed between DO and pH values (Table 4). The value of COD in the present study ranges from 1.60 - 9.60 mg/L at site 1B and site C respectively. There was no standard limit set for COD by WHO and EGL. However the COD values obtained for Gomo and Guracho streams water in the present study were not greater than the Pakistanian standard limit of COD value (10 mg/L) for drinking purpose [36].

Total Hardness: Hardness values of the water samples in the streams water of the present study varied from 2.64 - 3.34 mg/L Ca and Mg as CaCO_3 , which was soft and fit for drinking purpose. According to the WHO standard for drinking purpose, total hardness less than 60 mg/L Ca and Mg concentration as CaCO_3 was considered as soft water and for domestic uses (washing and cooking) hardness should be less than 200 mg/L Ca and Mg concentration as CaCO_3 [33].

Table 5: Mean values±SD of heavy metals concentration of the streams water with drinking and agricultural quality standard of WHO (2011), Ethiopian Guideline (EGL) and FAO

Para (mg/L)	(Site 1A)	(Site 1B)	(Site 2A)	(Site 2B)	(Site C)	WHO	EGL	FAO
Fe*	0.55±0.03	0.47±0.02	0.53±0.02	0.19±0.04	0.11±0.001	0.30	0.20	5.00
Cr	0.14±0.05	0.06±0.02	0.09±0.01	0.11±0.07	0.02±0.001	0.05	-	0.10
Cu*	0.14±0.09	0.26±0.06	0.09±0.01	0.07±0.01	0.01±0.001	2.0	2.0	0.20
Mn*	0.63±0.16	0.39±0.12	0.19±0.01	0.11±0.03	0.03±0.007	0.50	0.50	0.20
Zn*	0.54±0.04	0.37±0.05	0.63±0.05	0.41±0.01	0.09±0.02	3.00	5.0	2.00

Parameters indicated by * are significantly different among sites ($p < 0.01$), SD- standard deviation, para.- parameters, sites 1A-Guracho upstream, 1B- Guracho downstream, 2A- Gomo upstream, 2B- Gomo downstream, FAO - Food and agricultural organization

Analytical Data of the Heavy Metals

Iron (Fe): Data obtained from the present study indicated that the minimum (0.11 mg/L) and maximum (0.55 mg/L) concentration of Fe were found respectively at site C and site 1A. However the mean values of Fe concentration decreases down the streams in both Guracho and Gomo streams (Table 5). This may be due to the fact that sites 1A and 2A were sites very close to Tulu Kapi gold mining activity.

The average mean Fe concentration recorded in rainy and dry seasons were 0.46 and 0.29 mg/L (Table 3). This may indicates that there was higher discharge of Fe containing effluents washed to the nearby stream during rainy season than in dry season. Fe concentration showed negative correlation ($p < 0.01$) with pH values (Table 4). Data obtained from the present study showed that with increasing Feconcentration pH value of the streams water decreases. According to the WHO guide line for drinking water Fe concentration in water should not exceed 0.3 mg/L and as per the standard limit of EGL [34] it was less than 0.2 mg/L. In line with this, the Food and Agriculture Organization recommended the level of Fe in irrigation water to be 5 mg/L. Therefore, from the three sites (site1A, site 1B and site 2A), the concentration of iron was relatively greater than that of WHO and EGL for drinking purpose. Therefore, from the data of the present study it is possible to conclude that water from these sites was not suitable for drinking without any treatment.

Chromium (Cr): Results of the present study shows that the concentration of Cr ranged between 0.02 and 0.14 mg/L at site C and site 1A respectively. The United Nations Food and Agriculture Organization recommended maximum level of Crfor irrigation water was 0.10 mg/L. According to WHO primary drinking water standard, the maximum limit of Cr concentration was 0.05 mg/L. But as indicated in (Table 3), the average Crconcentration obtained in rainy and dry seasons were 0.14 mg/L

(Site 1A) and 0.11 mg/L (Site 2B) respectively, which were greater to small extent than the maximum limit of WHO guide line for drinking water.

Copper (Cu), Manganese (Mn) and Zinc (Zn): The concentration of Cu was found within the range of 0.07 and 0.26 Mg/L at site 2B and site 1B respectively (Table 5). The mean average of Cu concentration in rainy season and dry season were 0.13 and 0.09 mg/L respectively. There was also negative correlation value between Cu concentration and pH values (Table 4). The level of Cu was much below the permissible limit for drinking water as recommended by world health organization standard limit which was 2 mg/L. The FAO recommended maximum level of copper concentration for irrigation water was 200 µg/L. Therefore the streams water of Guracho and Gomo was not polluted in term of Cu at present study. The concentration of Mn decreases down streams in both Guracho and Gomo. The minimum (0.03 mg/L) and maximum (0.63 mg/L) Mn concentration was recorded at site C and site1A respectively. According to [1, 34] for drinking purpose, Mn concentration of water should not exceed 0.5 mg/L. The Food and Agriculture Organization recommended maximum level for Mn in irrigation water was 0.2 mg/L. The recorded data showed that Mn concentration decreased down the streams along with increasing pH values of the water. Result of the present study shows that in both Guracho and Gomo, Zn concentration decreases down the streams. The minimum (0.09) and maximum (0.54 mg/L) values of Zn concentrations were recorded at site C and site1A respectively (Table 5). The guide line set by world health organization for maximum Zn concentration in drinking water was 3 mg/L while the Food and Agriculture Organization recommended level for Zn in irrigation water was 2 mg/L [31]. Hence, at present study, water from Guracho and Gomo streams has acceptable concentration of Zn for both drinking and agricultural purposes.

CONCLUSIONS

The results of the present study showed that the values of turbidity obtained from all the selected sampling sites of Gomo and Guracho streams water were above the standard limits of WHO and EGL for drinking purpose. This might be due the land excavation and soil disturbance activity of Tulu Kapi gold mining project and continuous gold searching activity of some local residents around the streams. The concentration of Fe at sites 1A, 1B and 2A was also found to be beyond the standard limit of WHO and EGL during rainy seasons. This makes the water certainly unfit for drinking purposes without any form of treatment. But for various other surface water usage purposes, it still could be considered quite acceptable because all other quality parameters measured in the present study were in the recommended standard limit for drinking and agricultural usage set by WHO, EGL and FAO. The study also confirmed that there was no pollution source from other domestic wastes of rural areas and agricultural fertilizers that affected the streams water quality. The concentration of all the heavy metals analyzed in the present study increases upstream, together with decreasing pH value. This showed that there were some indications of the presence of acid mine drainage in the rainy season. However, the streams water was not seriously affected by acid mine drainage.

Data Availability: We used primary data. The primary data that we applied to support the findings of this study were new samples taken from the sampling sites. Hence, the conclusion of the present finding was accessed from parameters of the samples taken from laboratory results.

Conflict of Interest: The author declares that there are no conflicts of interest with regard to the publication of this original research paper.

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