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Assessing the Environmental Impact of Artisanal Gold Mining Activities on the Waters and Sediments Around Meli, Northwestern Tigray, Ethiopia

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ABSTRACT

The paper presents the environmental impact of artisanal gold mining activities on the waters and sediments around Meli, northwestern Tigray, Ethiopia. Stream sediment, water, and tailing samples were collected in the dry season in January of 2019 and analyzed for heavy metals Cu, Zn, Pb, and As. The physicochemical parameters (pH, EC, major cations, and anions) of a few water samples were also measured. Flame atomic absorption spectrometry was used to determine the level of the metals in stream sediments. The results show that tailing has the highest concentration of metals followed by the stream sediments. The least concentrations are recorded in water for all metals. Pb has the highest mean concentration of all heavy metals in stream sediments, waters, and tailing samples. The mean Geo-accumulation Index (Igeo) and Contamination Factor (CF) suggest that the sediment represents uncontaminated to moderately contaminated classes. Concentrations of Cu and Zn in the water samples are generally within the maximum allowable concentration of the WHO, whereas concentrations of Pb and As are above the limit. Metal Index for surface and groundwater suggests that the area is polluted with heavy metals Pb and As. The main sources of the metals are assumed to be the sulfide ores facilitated by natural weathering processes and artisanal mining activities like excavations, crushing, grinding, and amalgamation processes. The Gibbs and Durov plots show that major hydrogeochemical processes controlling the water chemistry are water-rock interactions with considerable mixing of water types.

Keywords: Artisanal gold mining, Water Pollution, Stream Sediment, Meli, Tigray, Ethiopia.

1. INTRODUCTION

Artisanal gold mining (AGM) refers to small-scale, largely informal mining activities for extracting gold from the ground and recover the gold using hand tools (Attua et al., 2014). Such mining operations have received special attention due to the release of heavy metals; generation of solid wastes and mercury contamination during gold processes (Malm et al, 1990; Salomons, 1995; Tarras-Wahlberg et al., 2000). Impacts of any mineral resource development range from physical destruction with accompanying the loss of bio-diversity resources to the accumulation of pollutants in different environmental media (Getaneh and Alemayehu, 2006). Environmental media polluted by heavy metals should be of great concern for several reasons such as their potential long-term effects on human health particularly in developing countries (Simeonov, 2003; Armah et al., 2010).

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In the northwestern Tigray, Asgede Tsimbla district, which includes the study area Meli, AGM is being conducted in 217 mining sites engaging large number of jobless youths (Meaza et al., 2017). The gold extraction has been carried out in the area in disorganized manner for many years (Meaza et al., 2015**)**. The AGM is extensive in Meli area and activities such as excavation; crushing, grinding and amalgamation are commonly practiced. The mining process is carried out without any environmental considerations (Getaneh and Alemayehu, 2006). The geochemical investigation of water and sediment is of major importance to understand the process leading to release of ions and metals. Water contamination is a common manifestation of mining activities (Remy, 2003). The accumulation of heavy metals in stream sediments can be a secondary source of water pollution once environmental condition is changed (Cheung et al., 2003). Hence, sediments can also be an environmental record of pollutants. AGM facilitates the release of heavy metals, mainly Hg, Pb and As to the environment (Asamoah, 2012). Copper, zinc, lead, and arsenic are chosen for the present investigation because the area is reported to host a base metal sulfide mineralization with auriferous quartz veins (Abraham et al., 2015; Bheemalingeswara and Atakilt, 2012). As and Pb are commonly associated in gold-sulphide deposits (Asamoah, 2012). The high degree of toxicity of arsenic and lead makes them of high public health concern (Tchounwou et al., 2012).

Since, there are no studies undertaken on the impact of AGM, a preliminary study was conducted to obtain baseline information on the possible impact of artisanal gold mining on the environment in Meli area. Thus, this paper is aimed to assess the artisanal gold mining process and its environmental impact by examining the metal distribution patterns and pollution indexing using water, stream sediment and tailing samples.

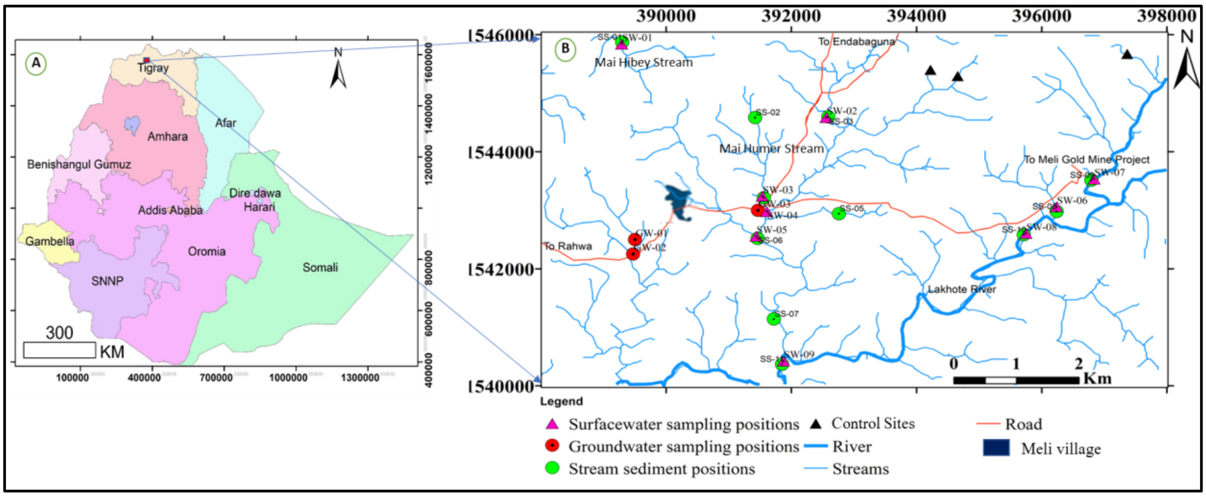

Figure 1. Location map of the study area showing the sample locations for waters and stream sediments.

1.1. Study Area

The study area covers about 60 km^2, around Meli and located in northwestern Tigray, northern Ethiopia (Fig 1). It is about 371 km from Mekelle, 61 km SW of Shire Indasillasie town. The area is having scarce vegetation cover and rugged topography. Temperature varies from 40^{o}C in the dry to 20^{o}C in wet season and experiencing 600-800mm annual rainfall. According to census 2007, the population of Asgede-Tsimbla district that encompasses the study area was 135,621 with high records of migrants who engage in traditional gold mining (Hagos et al., 2016).

2. METHODOLOGY

2.1. Sample Collection

Twelve water samples comprised of 9 surface waters (SW-01 to SW-09) and 3 shallow groundwater (GW-01 to GW-03) not exceeding 60m depth, were collected during dry season of January 2019 (Fig 1). The water samples were collected in pairs of l liter pre-washed polyethylene bottles. Before sampling, groundwater was pumped for several minutes to avoid the effects of stagnant water. The water samples collected for heavy metal analysis were preserved by acidifying with four drops of HNO_3 acid during sampling. The samples were labeled and kept at 4°C refrigerator prior to analysis. Sampling protocols were done according to the standard procedures (APHA, 1998). Parameters such as pH, electrical conductivity (EC) were recorded on the spot.

Fourteen stream sediment samples, 11 from affected stream sediments (SS-01 to SS-11) and 3 from unaffected upstream sediments were collected for comparison as control sites to set background from the unaffected upstream part of the study area, to distinguish the natural vs anthropogenic inputs. The control sites are also draining relatively the same country rocks i.e., mafic, felsic, and intermediate metavolcanics.

The samples were taken from the top surface layer of sediment at a depth of 0–20 cm after removing plant debris and gravels. About 1 kg of sediment sample was taken from single site using a shovel tool. The stream sediments were air dried in the field under a less windy environment. Samples were kept in pre-cleaned plastic bags and brought to Mekelle University geochemical laboratory.

Two artisanal mine tailing samples were collected from dumps of Amalgamation sites from northwestern and central part of the area. Part of the samples from one site were homogenized together to obtain a representative sample of the tailing. About 1kg of each tailing sample was collected using a shovel tool. They were retained in pre-cleaned plastic bags and transferred to Mekelle University geochemical laboratory.

2.2. Sample Preparation

For extraction of heavy metals from the tailing and stream sediment samples, two methods of digestion techniques were employed in this study. Partial digestion (acetic acid extraction) for stream sediments following the method proposed by the United Nations Environment Programme (UNEP, 1995; Peña-Icart, 1995) and Semi-total (aqua regia) digestion for tailings in accordance with Examination of Water and Wastewater (APHA, 1998). Acetic acid extraction is typically employed for environmental analysis where complete dissolution is either not required or is undesirable and the goal is to determine extent of heavy metal contamination originating from anthropogenic activities (Loring and Rantala, 1992; UNEP, 1995).

2.3. Sample Analysis

The chemical analyses of (water, stream sediment and tailing) samples were carried out in Mekelle University Hydrogeochemical laboratory. Twelve water samples were analyzed for 4 heavy metals (Cu, Zn, Pb, and As). 7 of the 12 water samples were selected for major cations ($Ca^{2+,}$ Mg^{2+}, Na^+ and K^+) and major anions (HCO_3^-, NO_3^-, Cl^- and SO_4^{2-}) analysis. A total of 11 stream sediment samples were analyzed for 4 heavy metals (Cu, Zn, Pb, and As) using Atomic Absorption Spectrophotometer (Varian Spectrometer AA-400). AAS settings are provided in table 1. Apart from heavy metals, Ca and Mg were also analysed using AAS while Na and K were analyzed using the advanced Flame photometer (model, PFP7). Titration and UV-spectrophotometer analytic methods were used for the analysis of HCO_3^-, NO_3^-, Cl^- and SO_4^{2-} in water samples. Digital handheld pH-meter was used to measure the pH and electrical conductivity (EC) of the water samples. The analyses were carried out in accordance with the Standard Method for Examination of Water and Wastewater (APHA, 1998).

Table 1. The wavelength and detection limit of the AAS for analysis of metals.

Metals	***Wavelength (nm)***	***Detection limit***
Cu	324.8	0.03 mg/l
Zn	213.9	0.05 mg/l
Pb	217	0.05 mg/l
As	193.7	0.01 mg/l

2.4. Quality Control

The precision of the analysis result is found <10% for metals and < 5% for cations and an ions. To check precision each sample was run repeatedly and randomly. Finally, the average of the triplicate readings was taken for each sample (Table 2). To validate the quality of water analyses, ionic balance error (electro neutrality) was computed. It was computed as the equation given below (Appelo and Postma, 2005). The EN value for surface and groundwater is 4.59% and 0.8% respectively.

Electro neutrality (EN%)=$\frac{\Sigma \text{ Cations}-\Sigma\text{Anions}}{\Sigma \text{ Cations}+\Sigma\text{Anions}}\frac{\Sigma \text{ Cations}-\Sigma\text{Anions}}{\Sigma \text{ Cations}+\Sigma\text{Anions}}$ *100 (ionic concentrations in meq/l)

Table 2. CV% randomly selected (SS-06) triplicate analysis.

Metal	***Concentration (mg/l)***			***Mean***	***SD***	***CV (%)***
	Reading 1	***Reading 2***	***Reading 3***			
Cu	30.4	31.21	28.03	29.8	1.6	5.37%
Zn	7.4	8.3	8.4	8	0.5	6.88%
Pb	57	61.5	67.8	62.1	5.42	0.09%
As	7.3	7.2	7.6	7.4	0.2	2.7%

2.5. Data Treatment

Software's such as ArcGIS 10.4.1, Surfer 10, and Global mapper 12 were used for data processing of environmental geochemical mapping. The water quality parameters were compared with WHO (2018) and ES (2013) standards to evaluate its suitability for drinking purpose. Statistical software like (SPSS) 20.0 was used for descriptive statistics and Pearson correlation analysis. Hydrochemistry diagrams such as Durov diagram (prepared through AquaChem software) and Gibbs diagrams were used to identify source of dissolved ions. Pollution indices were employed to assess the level of sediment and water contamination. The types of indices are chosen according to the availability of data (Appendix 1).

3. GEOLOGY AND MINERALIZATION

3.1. Geology of the Study Area

The geology of the study area is mainly composed of mafic, intermediate and felsic metavolcanics, intermediate metavolcaniclasts (MVC), phyllite and intrusive rocks (Fig 2). The mafic metavolcanic rock is widely available in the northwestern, eastern and southern parts of the study area. The intermediate metavolcanic rock is mainly exposed in southern, central and eastern parts whereas the felsic metavolcanics are confined to the northeastern part. Phyllite unit is outcropped along E-W in contact with mafic metavolcanic and intermediate metavolcanic rocks. Granite is exposed in northern and southern parts of the study area.

3.2 Mineralization and Artisanal Gold Mining (AGM)

Gold occurs in the area in quartz veins which are traversing different rocks, and as byproduct in volcanogenic massive sulfide (VMS) mineralization which is mainly confined to intermediate metavolcanic rocks (Abraham et al., 2015; Bheemalingeswara and Atakilt, 2012).

In addition, gold occurs in the gossan developed on VMS and as placer. During AGM, gold is mainly recovered by crushing the gold- bearing primary rocks, quartz veins and sulfides from the surface apart from placer gold from stream channels. The artisanal gold miners conduct both alluvial mining and hard rock mining. The hard rock gold is recovered by crushing with chisels and hammers followed by grinding and amalgamation processes. In hard rock extraction, the traditional miners access the gold bearing quartz vein through tunnels, and then follow the vein. Currently, artisanal gold extraction from primary rocks is more active than mining from alluvial sediments.

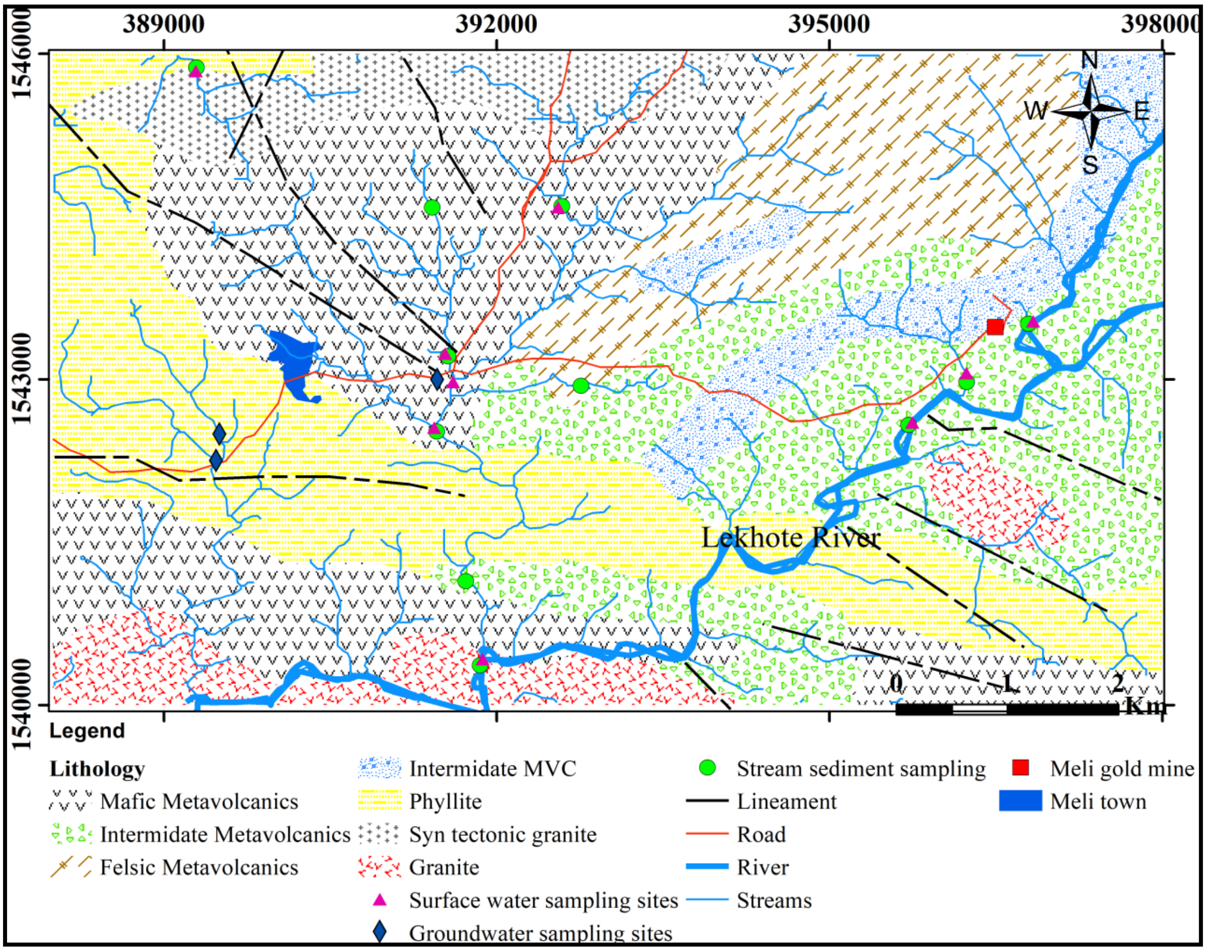

Figure 2. Geological map of Meli area (Modified from EMD, 2007 and Abrham et al., 2015).

Gold recovery is carried out by combining the elemental mercury with grinded ore. Tremendous amount of mercury was used to amalgamate the gold; this is caused by the miner's erroneous belief that the more mercury used the greater the rate of gold recovery. The local miners burn the amalgam mostly at the site, sometimes at residence. Alluvial gold (placer gold) on the other hand is found along the stream beds, older stream channels and flood plains. In addition to gold-bearing quartz veins, VMS deposit is expected to contribute Cu, Zn in significant quantities compared to Pb and As. According to Abrham et al. (2015), the sulfide mineral assemblage present in VMS is pyrite, chalcopyrite, sphalerite, and galena in the order of abundance.

4. RESULTS AND DISCUSSION

4.1. Stream Sediments Characteristics

The analytical results of heavy metals in stream sediments (ppm) and in the reference/control site are presented in table 3. Their spatial distribution in stream sediment samples is shown in (Fig 3). The result shows that mean concentration of copper in the stream sediment is 18.92 ppm. It ranges from 1.3 to 45 ppm. Approximately 54% of the samples exceeded the reference stream sediment value of Cu 6.1 ppm. The highest concentration of Cu (45ppm) is recorded at Lekhote River (SS-10) after Maiserakit stream joins Lekhote River. The elevated values could be attributed to the presence of the typical minerals for copper (e.g., chalcopyrite). Lowest value (1.3ppm) of copper concentration is measured in (SS-05) which is collected below a very recent alluvial mining site. Cu concentrations in the downstream (SS-11) could be due to very low mobility of Cu in alkaline conditions, where the pH of the solution ranges from 7.34 to 8.42. The spatial distribution of copper in the stream sediment samples over the study area is shown in (Fig 3).

The concentrations of zinc in the stream sediment samples range from 5.1ppm to 32.4 ppm and with mean value of 11.32 ppm. Over 72% of the samples give lower zinc values compared with the reference sediment value of 10 ppm (Table 3). The highest value of zinc concentration (32.4 ppm) is obtained in a sample (SS-04) taken near intensive ore processing site. The source of the high zinc concentration is possibly related to the presence of minerals like Sphalerite in the gold ore released by the artisanal mining activities (Abrham et al., 2015). Low value of zinc 5.1 ppm is obtained from sample (SS-05) is taken from a stream below very recent alluvial mining site.

Table 3. Heavy metals concentration in stream sediments (ppm).

Sample ID	***Cu***	***Zn***	***Pb***	***As***
SS-01	3	14.3	2.3	8.4
SS-02	26	5.6	48.5	16.6
SS-03	32.5	8.6	42	5.3
SS-04	5.6	32.4	3.2	15.7
SS-05	1.3	5.1	2.7	15.2
SS-06	29.8	8	62.1	7.4
SS-07	4.8	9.7	3.3	18.8
SS-08	21.9	7.4	41.5	19.5
SS-09	34.3	9.5	52.5	11.1
SS-10	45	7.2	62.2	8.4
SS-11	3.9	16.7	2.5	16.6
Min	1.3	5.1	2.3	5.3
Max	45	32.4	62.2	19.5
Mean	18.92	11.32	29 .35	13
SD	15.6	7.8	26	5
Mean in RS	6.1	`10	4.8	10.4

SD=Standard deviation, RS=Reference sediment, Nm=Not measured

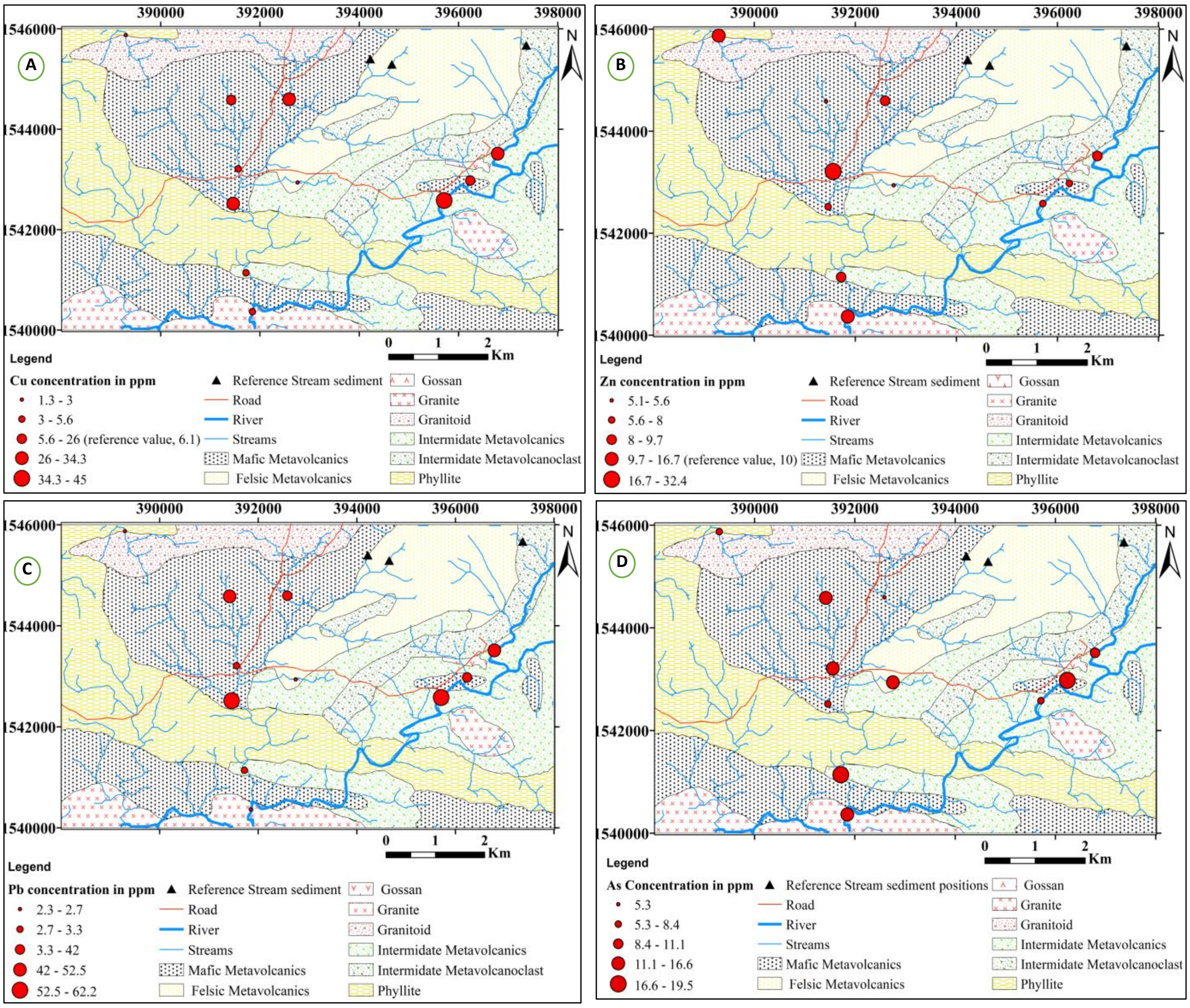

Figure 3. Spatial distribution maps of the metals in stream sediments A) Copper, B) Zinc, C) Lead and D) Arsenic.

Lead concentration varies from 2.3 ppm to 62.2 ppm with mean value of 29.35 ppm. 54% the sampling sites show higher values as compared to the stream sediment reference value of Pb 4.8 ppm (Table 3). Generally, referring to the environmental geochemical map (Fig 3), Pb is concentrated around its sources maybe due to the very low mobility of the metal in neutral to alkaline conditions. The highest lead concentration (62.2 ppm) is obtained in stream sediment sample (SS-10). The next higher lead content (62.1 ppm) is recorded in a sample (SS-06) taken from the near intensive artisanal gold processing site. This might be due to leaching of minerals like galena during processing and/or lead containing secondary minerals in the washed gold ore. Very low Pb values observed could be due to minor amounts of galena present in the source rocks (SS-01).

The contents of As in the stream sediments varies between 5.3 and 19.5 ppm with mean value of 13 ppm, which is higher than the amount of As in reference stream sediment (10.4 ppm) (Table 3). Over 54% of the stream sediment samples give higher values as compared to the reference value. Thus, high levels of As obtained in stream sediments are derived from the artisanal gold mining activities. Furthermore, Meli gold ore processing plant may be an additional source of arsenic as indicated in sample (SS-08). Thus, higher value can be attributed to weathering of waste rock dumps and runoff of discharged effluents from the ore processing plant. Figure 3 shows the spatial distribution of arsenic in stream sediment samples. The mineralized rocks of the study area, Metavolcanic rocks, contain higher contents of Cu, Zn and Pb (Abraham et al., 2015).

4.1.1. Heavy Metal Pollution

The calculated mean Igeo values are 0.4, -0.6, 0.9 and -0.39 for Cu, Zn, Pb and As respectively. Based on the average Igeo values, the ranking of intensity of heavy metal pollution of the stream sediments is as follows: Pb >Cu >As >Zn. According to Muller (1969), Igeo value ranged from 0 (unpolluted) to 1 (unpolluted to moderately polluted). As and Zn were found in the unpolluted (Igeo<=0), it demonstrates that sediment is near the background value. Cu and Pb have the Igeo value between 0 and 1 which falls in (0< Igeo < 1). This indicates that the stream sediment is uncontaminated to moderately contaminated at most of the sites. Generally, the stream sediment is not contaminated by Zn and As at present. However, the trend shows that the concentrations will increase in the future.

The calculated mean CF values are 3.1, 1.1, 6.1 and 1.2 for Cu, Zn, Pb and As, respectively. Based on the average CF values, the ranking of intensity of heavy metal pollution of the stream sediments is as follows: Pb >Cu >As >Zn. According to Hakanson (1980) classification, stream sediments in the study area are moderately to very highly contaminated.

The stream sediment has moderate metal contamination factor (CF) values for Zn and As, considerable CF values for Cu and very high CF value for Pb.

The calculated mean value of contamination degree for all the sites is 11.5. CD is found highest at SS-10 (21.86) and lowest at SS-05 (2.73). In accordance to the Ahdy and Khaled classification, the mean value CD sediment value fall in ($6 \leq CD < 12$) which indicates the stream sediment sampling sites are moderately contaminated.

Pollution load index (PLI) values of sediments of all the studied sites range between 0.5 and 2.8. In accordance to Tomlinson et al. (1980) and Chakravarty and Patgiri (2009), the PLI < 1 for sites (SS-01, SS-05, SS-07, SS-11) with 36.36% of the samples indicating no pollution i.e. metals are of geological origin) and 63.64% of the samples have PLI >1 suggesting that the stream sediments of those samples are progressively polluted (anthropogenic inputs).The calculated mean PLI sediment value of the samples was found to be polluted (2.24), PLI > 1 suggesting inputs from anthropogenic sources are significant. Pollution load indices were found to increase near to the intensive artisanal mining activities.

The potential risk factor for individual metals in the stream sediments is in the sequence of Pb (30.5) > Cu (15.5) >As (12) >Zn (1.1). The calculated potential ecological risk index (RI) value of total heavy metals is 59.1. According to Hakanson (1980) the grading standards, sampling sites are at low risk level where the RI is lower than 150.

4.1.2. Correlation Analysis of Metals in Stream Sediments

The Pearson correlation analysis for the studied metals (Cu, Zn, Pb and As) is done for the stream sediment samples (n=11) at 95% confidence level. The results obtained are -0.44 (between Cu and Zn), 0.96 (between Cu and Pb), -0.52 (between Cu and As), -0.51 (between Zn and Pb), 0.14 (between Zn and As) and -0.44 (between Pb and As). The very strong positive correlation obtained between the copper and lead (0.96) implies that they are possibly contributed to the stream sediment from the same source and having identical behavior during the transport process. The negative correlation among metals shows that the metals are not controlled by a single factor.

Table 4. Heavy metal analysis in tailings in (ppm).

Sample ID	**Cu**	**Zn**	**Pb**	**As**
Sample from NW part	20.4	56.1	51.6	48
Sample from central part)	97.6	35.2	285.5	26.5
Mean	59	45	169	37
Crustal Average (Taylor, 1964)	55	70	12.5	1.8

4.2. Geochemistry of Tailing

The analytical result of heavy metals in tailing material is presented in table 4. The tailing samples showed comparatively low levels of Zn and very higher levels of Cu, Pb and As compared to average crustal abundance values (Taylor, 1964) (Table 4).

4.3. Hydrogeochemistry and Water Quality

Tuzen et al. (2002) has classified physical pollution parameters such as (pH, electrical conductivity, and dissolved matter) and chemical pollution parameters (total hardness and different heavy metal ions present in water). In this context, this study evaluates the distribution of four heavy metals (copper, zinc, lead and arsenic), in situ measured parameters (pH and EC) and total hardness of water.

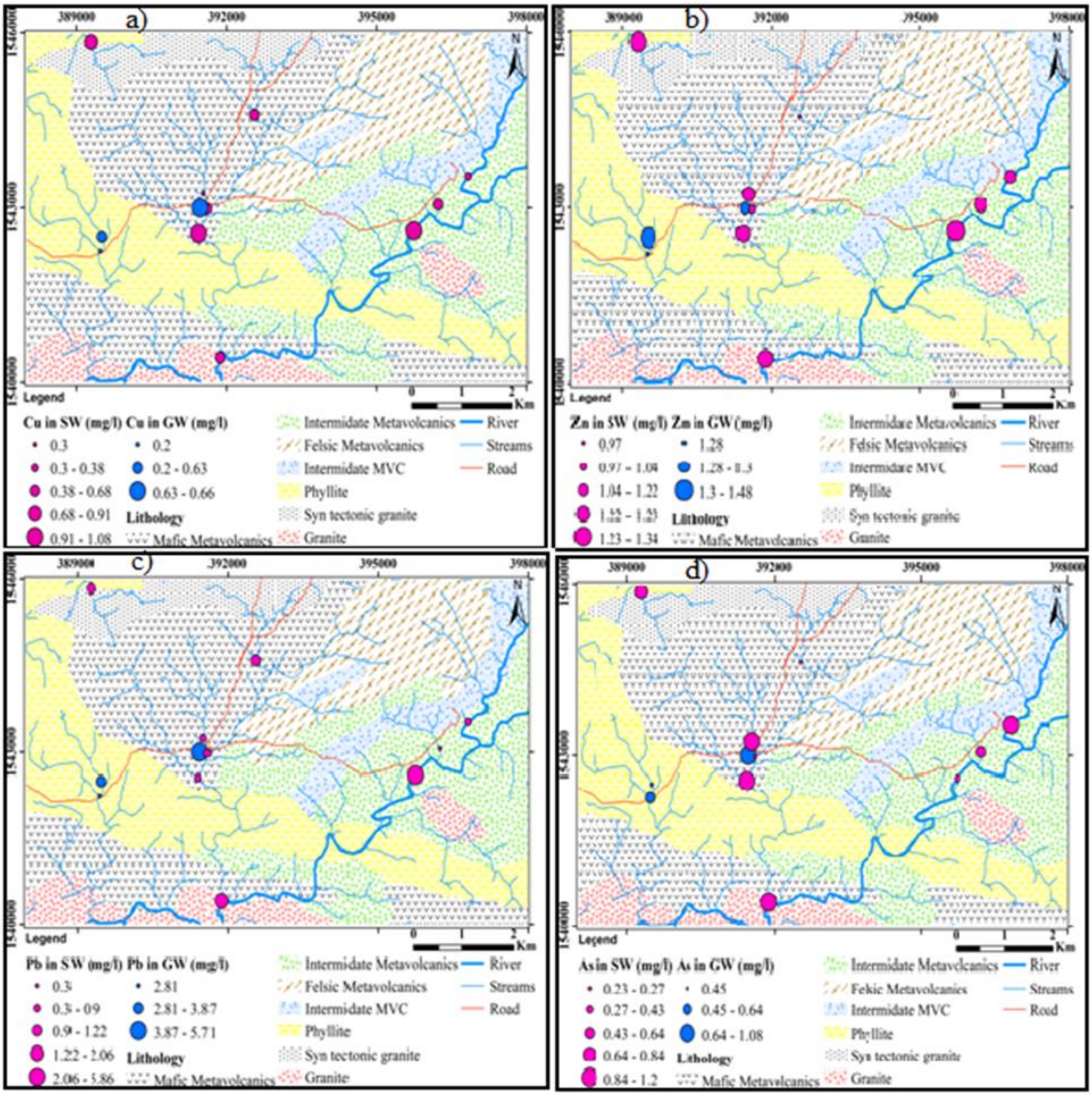

Figure 4. The spatial distribution maps of A) Copper B) Zinc C) Lead and D) Arsenic in surface and ground waters of Meli area.

4.3.1. Heavy Metal Concentrations in Waters

Figure 4 presents the spatial distribution maps of copper, zinc, lead and arsenic concentrations in surface and ground waters of Meli area. The concentration of copper in surface and groundwater samples ranges from 0.3-1.08 and 0.2-0.66 mg/l, respectively. The mean concentrations of Cu in surface and groundwater are 0.66 and 0.55 mg/l, respectively. All the water samples (100%) fall below Maximum Allowable Concentration (MAC) of Cu (2 mg/l). Zinc has mean concentration of 1.2 mg/l and 1.35 mg/l in surface and groundwater, respectively. It ranges from 0.97-1.34 mg/l in surface water and 1.28-1.48 mg/l in groundwater. All the water samples (100%) fall below MAC of Zn (5 mg/l) in the study area. The concentration of Pb varies in surface waters (0.3 to 5.86) and in groundwater (2.81 to 5.71) with mean values of 1.53mg/l and 4.13 mg/l respectively. All the water samples (100%) fall above MAC of Pb (0.01mg/l) in the study area. The highest content of Pb 5.86 mg/l in the surface water sample (SW-08) is recorded in the eastern part of the area. The arsenic concentration ranges from 0.23 to 1.2 mg/l in the surface water samples and 0.45 to 1.08 mg/l in the shallow groundwater samples. The mean values are 0.77 mg/l and 0.72 mg/l, respectively. All the water samples (100%) fall above permissible limit of As (0.01mg/l).

The Metal index (MI) is used to assess the level of heavy metal contamination in the water samples. The Ethiopian guideline for drinking water purpose is used as MAC of the metals. The higher the concentration of a metal compared to its MAC value the worse is the quality of water. The calculated mean MI values for Cu, Zn, Pb and As in surface water are 0.33, 0.24, 153 and 77 and in groundwater 0.25, 0.27, 413 and 72, respectively. According to Lyulko et al. (2001); and Caerio et al. (2005), the water with respect to Cu and Zn is considered as suitable for drinking purpose because (threshold limit of MI value <1) whereas the water is unsuitable for drinking purpose with respect to Pb and As since (threshold limit of MI value >1). Referring to maps in (Fig 4), sources of metal pollution in the central part of the study area are found to be waste rocks, tailings resulted from the activities of artisanal gold extraction and weathering of the massive sulphide deposit in the eastern part of the area. The metals are unlocked from the host minerals/rocks and released to the environment by natural weathering as well as human activities, like mining-crushing, grinding, leaching etc (Getaneh and Alemayehu, 2006).

4.3.2. Physicochemical Characteristics

The analytical result of major cations and anions of surface and ground water is presented in table 5. The pH of the surface waters ranges from 7.34 to 8.42 having mean value of 7.85 and in groundwater varies from 6.87 to 6.93 with mean value of 6.9. All are within the permissible limit range of 6.5–8.5 (WHO, 2018). The electrical conductivity (EC) values ranges from (604-1888 μS/cm, mean of 1178μS/cm) and (955-1451 μS/cm, mean of 1203 μS/cm) in surface and groundwater, respectively. The lower concentration values of EC lies in the eastern side, whereas, the higher concentration values of EC lies in the central part of the study area. The highest EC corresponds to higher ionic concentration caused due to artisanal extraction processes that release ions into the water. Compared to the other sampling points, groundwater (GW-03) recorded high conductivity values. Since these sampling points are near the intensive artisanal gold processing site, it is possible seepage of effluent discharges.

The range of concentration for (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) in the surface water samples is 46-144 mg/l, 19-37 mg/l, 38.7 mg/l and 1.6-2.1 mg/l and groundwater samples, 112-132 mg/l, 22-29 mg/l, 36.7-40 mg/l and 2.93-4.45 mg/l, respectively (Table 5). Among cations calcium is most dominant cation in study area followed by Na. Values for the bicarbonate, chloride, sulphate and nitrate in the surface water samples ranges from 231.8-396.5 mg/l, 63.2-80.55 mg/l, 65-160 mg/l and 3.33-11.36 mg/l and in groundwater ranges from 256.2-280.6 mg/l, 41.5-47.05 mg/l, 182-230mg/l and 9.69-11.81 mg/l, respectively (Table 5). The bicarbonate is the most abundant due to natural weathering process.

Table 5. Concentration of major cations and anions (mg/l) and standards in surface and groundwater samples.

Parameter	***SW-01***	***SW-03***	***SW-04***	***SW-07***	***SW-08***	***Mean***	***GW-02***	***GW-03***	***Mean***	***WHO, 2018***	***ES, 2015***
Ca	102	140	144	46	49	96.2	112	114	122	75	75
Mg	27	37	33	19	20	27.2	22	29	25.5	50	50
Na	38.7	44.7	49	40	41.7	42.8	36.7	40	38.35	200	200
K	1.6	1.8	0.48	2.1	2.1	1.6	2.93	4.45	3.69	1.5	1.5
HCO_3	396.5	359.9	359.9	262.3	231.8	322	280.6	256.2	268.4	500	500
Cl	63.2	67.83	71.27	70.83	80.55	70.75	47.05	41.5	44.28	250	250
SO_4	106.3	155.3	160	65.4	86.9	114.6	181.6	230.1	206	250	250
NO_3	11.36	9.69	10.76	10.12	3.33	9.05	11.81	9.69	10.75	50	50
pH	7.61	7.48	7.34	8.42	8.42	7.85	6.93	6.87	6.9	6.5-8.5	6.5-8.5
EC	1048	1715	1888	604	633	1178	955	1451	1203	50-1500	-

ES= Ethiopian standard, WHO=World health organization.

4.3.3. Mechanism controlling geochemistry of water

Gibbs (1970) diagram provides three distinct fields such as precipitation, evaporation, and rock–water interaction dominance areas. Gibbs diagram represents key processes controlling the surface and groundwater chemistry rather than origin. The Gibbs diagrams plots TDS versus Na/ (Na+Ca) (a) for cations and TDS vs. Cl/ (Cl+HCO_3) (b) for anions in figure 5. The plot suggests that the major mechanism controlling the chemistry of the waters of the study area is the chemical weathering of the minerals in the rocks. This implies that the water composition is influenced mainly by the water-rock interaction.

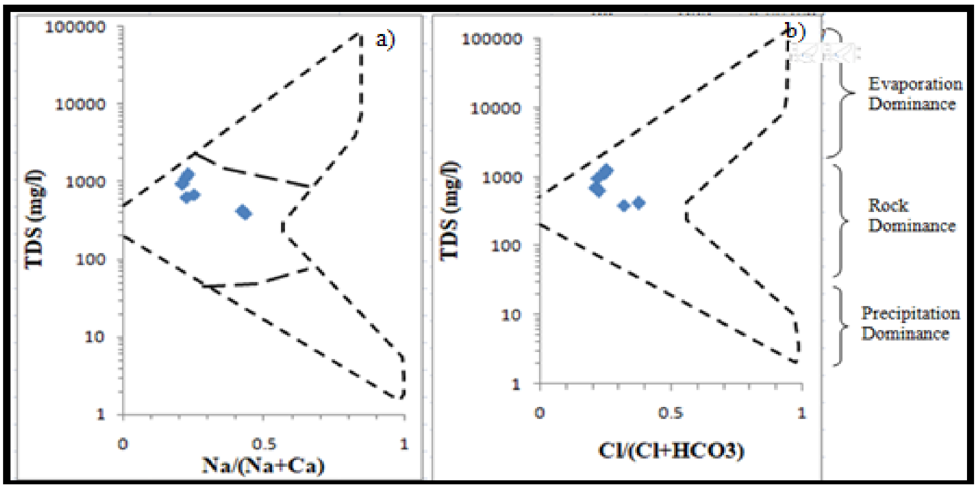

Figure 5. (a) Plots of log TDS versus Na/ (Na+Ca) and (b) log TDS versus Cl/ (Cl+HCO_3) (after Gibbs, 1970).

Durov diagram provides more information on the hydrochemical facies by helping to identify the water types and the possible geochemical processes that controls water genesis (Ghoraba and Khan, 2013). The major cations and anions of water samples were plotted in the Durov diagram and fell along the dissolution or mixing line which suggests that the waters undergo dissolutions (water-rock interactions) and mixed with pre-existing waters (Fig 6). As per this geochemical process, two chemical types of surface water and groundwater were recognized in the study area. The surface water type was changed from Ca-Mg-HCO_3-SO_4 (central part) to Ca-Na-Mg-HCO_3-Cl-SO_4 (eastern part). The groundwater samples were characterized as Ca-HCO_3-SO_4 (western part) and Ca-Mg-SO_4-HCO_3 (eastern part).

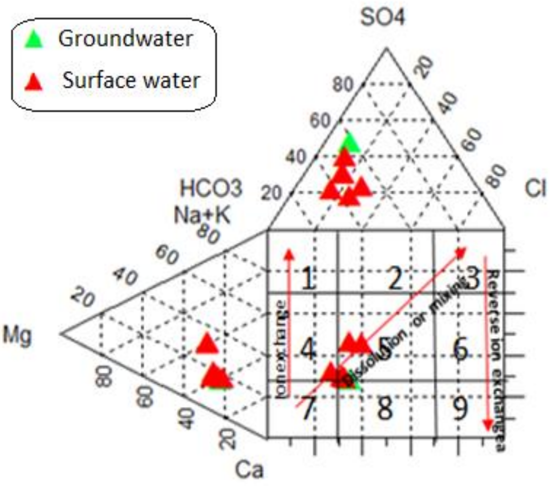

Figure 6. Durov plot depicting hydrochemical processes along the water types.

5. CONCLUSION

The findings reveal that lead has the highest mean concentration in stream sediment, water and tailing samples of the area. Depending on the amount of the CF value, lead appears to be the most harmful metal as it has a peak CF value of 6.1 in stream sediments. The average pollution load index (PLI) sediment value confirms that inputs from anthropogenic sources are significant. Based on the evaluation of physico-chemical parameters, it could be concluded that the artisanal gold mining activities in the central part of the study area has impacted the water quality. Metal index of the waters show that the water samples are critically contaminated with respect to heavy metals (As and Pb) in which the MI value was far above the threshold limit of 1. The higher concentration of heavy metals was detected along the streams where the separation mined minerals was carried out (gold ore processing sites). The main sources of metals are assumed to be sulfide minerals i.e., chalcopyrite ($CuFeS_2$) for copper, galena (PbS) for lead and sphalerite (ZnS) for zinc and arsenic may be found as impurities in these sulphide minerals. Mining activities such as excavation, crushing, grinding and amalgamation process can greatly enhance the release of the metals from their host rocks/ ore minerals. The study has indicated the potential of artisanal gold mining to harm the environment with heavy metals pollution and the need of further study on the impact in different environmental media.

6. ACKNOWLEDGEMENTS

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7. CONFICT OF INTEREST

There are no conflicts of interests.

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Appendix 1. Summary of geochemical indices used in the present study.

Media	***Geochemical indices***	***Equations***	***Pollution Levels***
Water quality	Metal Index (MI) (Tamasi and Cini, 2004; Caerio et al., 2005).	$MI = (C_i)/(MAC)_i$, Where MI is the metal index, MAC is maximum allowable concentration for each metal (ES, 2013 was used) and C_i is mean concentration of each metal.	Very pure: <0.3, Pure: 0.3-1. Slightly affected: 1-2, Moderately affected: 2-4, Strongly affected: 4-6, Seriously affected: >6.
Sediment quality	1. Geo-accumulation-index (Igeo) (Muller, 1979)	$Igeo = \log_2(\frac{CN}{1.5BN})$ Where CN is the measured metal in sediments, BN is metal in reference sediment, N both indicates same sediment size fraction (<2mm) and1.5 is correction factor, due to litho logical variations.	Unpolluted:($Igeo \leq 0$), No to Moderately: ($0 < Igeo < 1$), Moderately: ($1 < Igeo < 2$), Moderately to Strongly: ($2 < Igeo < 3$), Strongly: ($3 < Igeo < 4$), Strongly to extremely: ($4 < Igeo < 5$), and Extremely: ($Igeo > 5$) polluted.
	2. Metal contamination factor (CF) (Hakanson, 1980)	CF=Metal-concentration in sediments/referencevalue of the metal	Low: ($CF < 1$), Moderate:($1 \leq CF < 3$), Considerable: ($3 \leq CF < 6$), and Very high: ($CF \geq 6$). Contamination.
	3.Contamination degree (CD) (Ahdy & Khaled, 2009)	Sum up of all CF values of an individual sampling site	Low ($CD < 6$), moderate ($6 \leq CD < 12$), considerable ($12 \leq CD < 24$) and very high ($CD \geq 24$). Contamination.
	4. Pollution load index (PLI) (Tomlinson et al., 1980)	The PLI for a single site is the nth root of n number multiplying the factors (CF values) $PLI=\sqrt[n]{(CF1 * CF2 * CF3 \ldots CFn)}$ Where CF is the mean contamination factor and n is the number of metals (four in present study).	No pollution: PLI < 1 Progressively polluted: PLI >1
	5. Ecological risk index (RI) Hakanson, 1980	$RI = \sum_{i=1}^{n} Er = \sum_{i=1}^{n} Cf * Tr$ where CfCf is the contamination factor for the element, Er, individual potential risk factor TrTr, toxicity effect coefficient with values of Cu= Pb = 5, Zn = 1 and As = 10. RI is the total potential ecological risk of individual heavy metals in sediments.	Low: RI <150, Moderate: 150 < RI<300, High: 300 < RI<600, and significantly high: RI ≥ 600, ecological risk.