Geological and Geochemical Investigation of Low Grade Basement Rocks: Implication to Human Health in and around Asgeda Tsimbla, Western Tigray, Northern Ethiopia

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Abstract

The increase in the number of liver related disease patients from north western region of Ethiopia has been an environmental health issue of national concern. As the disease is restricted to a specific geographical terrain, particularly to Shire area, northwestern dry zone of the country, detail research studies are required to identify possible etiology and risk factors. The aim of the study is to determine the level of trace element and heavy metal concentrations and distributions in water and stream sediments of the area and identify the possible sources in relation to human health. During the study, geochemical sampling (20 water, 20 stream sediment and 6 rock samples) was carried out in March 2011. The collected samples were analyzed for their major and trace element contents using ICP-MS, ICP-OES, Ion Chromatography (IC), and XRF. Analytical data were organized and treated using Excel, SPSS, ArcGIS and Aquachem softwares. Analytical data results with respect to trace element contents in surface and ground waters are compared with the Maximum Acceptable Concentration or Maximum Allowable Concentration (MAC) of World Health Organization (WHO) and Ethiopian standards for drinking water. The comparison reveals that there are problematic elements that pass over the quality standards set for drinking water. One of these is: Bromine (Br), for which 100% all samples have value above 0.01 mg/l and up to 1.475 mg/l. Other problematic elements including aluminum (Al)—30%, fluorine (F)—20%, arsenic (As)—10%, and nitrate (NO_3)—10% are examples of elements which have above WHO-MAC for drinking water. Selenium (Se) deficiency may be the other problematic element in the area for its deficiency is associated with liver damage and heart muscle disorder. The metal contaminations (*i.e.* heavy metals) were also evaluated by world geochemical background value in average shale and sediment quality guideline proposed by US EPA. The concentration of Co and Cr exceeded average shale

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value at most sample stations indicated that these stations ware in potential risk. Geochemical factors are mostly considered to explain the etiology of this liver related disease.

Keywords

Liver Disease, Environmental Health, Geochemical Survey, Maximum Acceptable Concentration (MAC)

1. Introduction

Concern over the health of residents of northern Ethiopia—Shire area has been rising in recent years. Health professionals and members of the general public have watched people grow sick with variety of illness; particularly liver related diseases. Interviews with the local people indicated that the liver related diseases were identified in the area since 1980; about 70 people or more have been died so far. Males and females have been equally affected and children aged between 7 and 15 appear to be the most susceptible. With time the rate of disease is increased and affected more people.

In 2006 the Tigay regional Health Bureau sent national task forces (from Ethiopian Health Nutrition and Research Institute (EHNRI), and Addis Ababa University (Tukur Ambessa Hospital) into the area to investigate the cause of this disease. They took plant samples and it was analyzed by national EHNRI laboratory. The result interpreted as a potential toxic plant called "Ageratem" growing around the water source. The "Ageratem" contained a pyrrolizidine alkaloid and the "Gua Kua" disease was a Venue-Occlusive Disease (VOD) of the liver. As a result of this report the water supply in Tsada Emba—north eastern Shire—was filled in and the people internally displaced into the resettlement area in Kelakil—south eastern Shire [1].

No reduction in incidence was noted after the resettlement program. The Tigray health Bureau was forced to question the diagnosis, which led in turn in 2008 to a request to United State Center for Disease Control (CDC) to investigate the crisis in the area. They conducted a case control study and took serum samples, and concluded their report with Schistosomiasis as causative agents [2].

Oasis Foundation of Ethiopia (OFE) made contact with Imperial College of London who ran the Schistosomiasis Control Initiative (SCI). SCI sent a team to investigate a Schistosomiasis, and took (nail, stool and urine) samples and were able to conclude convincingly that Schitosomiasis was not a cause of morbidity [2]. Reports from EHNRI, CDC and SCI was reviewed by professor Thursz from Imperial Collage of London and agreed with the EHNRI reports that the most likely cause would be a Pyrrlizidine alkaloid as originally described with bush tea disease in Jamaica. However, it seemed unlikely that either "Ageratem" or the water supply could be a Pyrrlizidine alkaloid [2].

Since then detail multidisciplinary studies have been conducting to understand the problem from differ scientific point of view and might be resulting in an effective outcome.

In the study area there are abandoned and ongoing artisanal gold mining sites. Many individuals have been panning for gold using manual operations for a long time and there are many intermittent streams in the area into which drainage from gold mining sites flow into main rivers, and this may have led many people to ask whether the illnesses in the community have an environmental cause.

For the protection and conservation of water resource in the study area it is found to be important to characterize the quality of water. Ground water contamination with arsenic, fluoride and nitrate recently possesses serious health hazards to large sector of communities all over the word [3]. Since sediments and suspended particles are important repositories for trace metals such as chromium, copper, molybdenum, cobalt and manganese, studying of sediments of the environment is also found to be vital for characterization of the quality of the environment of the artisanal gold mining sites in and around the study area.

Trace element concentrations in the natural water vary widely depending on the geochemistry of rocks in the immediate environment. Interactions of water and plants with rocks (and soils developed from them) dictate our intake of these elements [4]. So knowledge of rock types in a particular area can help find out potential health problem with concentration of particular elements.

The Survey Area

The study area is located about 355 km northwest of Mekelle, Tigray national state, Northern Ethiopia. Geographically it is located 1,550,000 - 1,570,000 m (14˚01'12" to 14˚11'54") north latitudes and 370,000 - 390,000 m (37˚47'48" to 37˚58'54") east longitudes (**Figure 1**). Access within the study area is possible through weathered road that connects Shire town to the study area.

The study area is characterized by semiarid to arid climate. The average annual temperature for the region in generally varies from 24˚C - 29˚C [5]. Records obtained show temperature maxima between 37˚C and 40˚C and minima of 15˚C to 19˚C. November and December are the coldest months.

The area is generally characterized by rugged topography in its southern and western parts. It has an overall topography that decreases from northeast towards southwest. Metavolcanic and Metagranite generally occupy the high ground while the Metasediments predominantly in the river valleys. The altitude ranges from 1340 to 860 meters above sea level. Streams are intermittent and often drain southwest direction. The drainage pattern is sub dendritic to well developed dendritics. The main streams in the study area are: Mai-Hammar, Mai-Teli, Mai-Weyle, Sembel and Fesfesay rivers.

2. Methodology

2.1. Sampling

Field was conducted during March 2010. The sampling sites of water and stream sediments were selected based on the distribution of potential pollutant sources.

In conjunction with sampling, close field observations were made on the types of geology, physical land degradation and traditional gold panning practise (**Figure 2**). Our sampling positions and supplementary information is presented (**Figure 3**).

Thirteen (13) ground water and Seven (7) surface water samples were taken from deep borehole, shallow hand dug wells, rivers and ponds. Each sample was collected in one-liter polyethylene bottle and the sampling
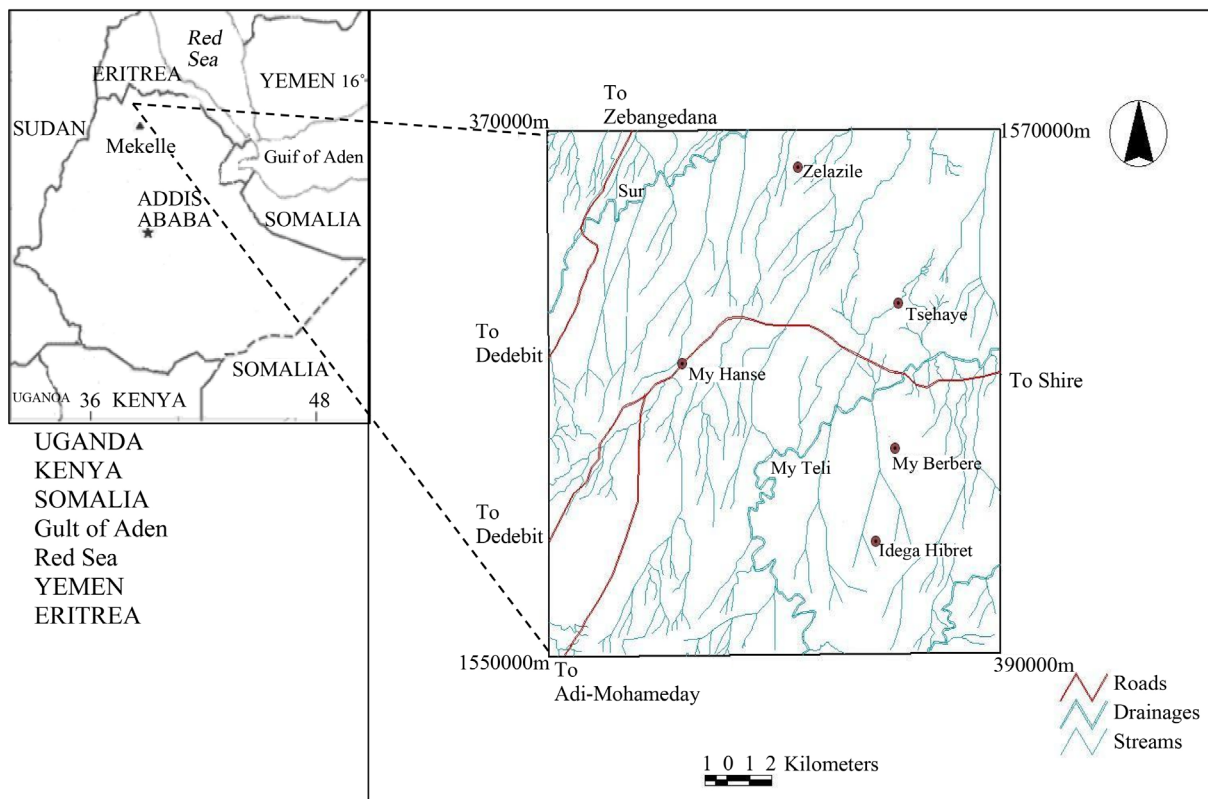

Figure 1. Location map of Asgede Tsimbla sub catchments area.

Figure 2. Artesinal gold mining practices in Asgeda Tsimbla sub catchment area.
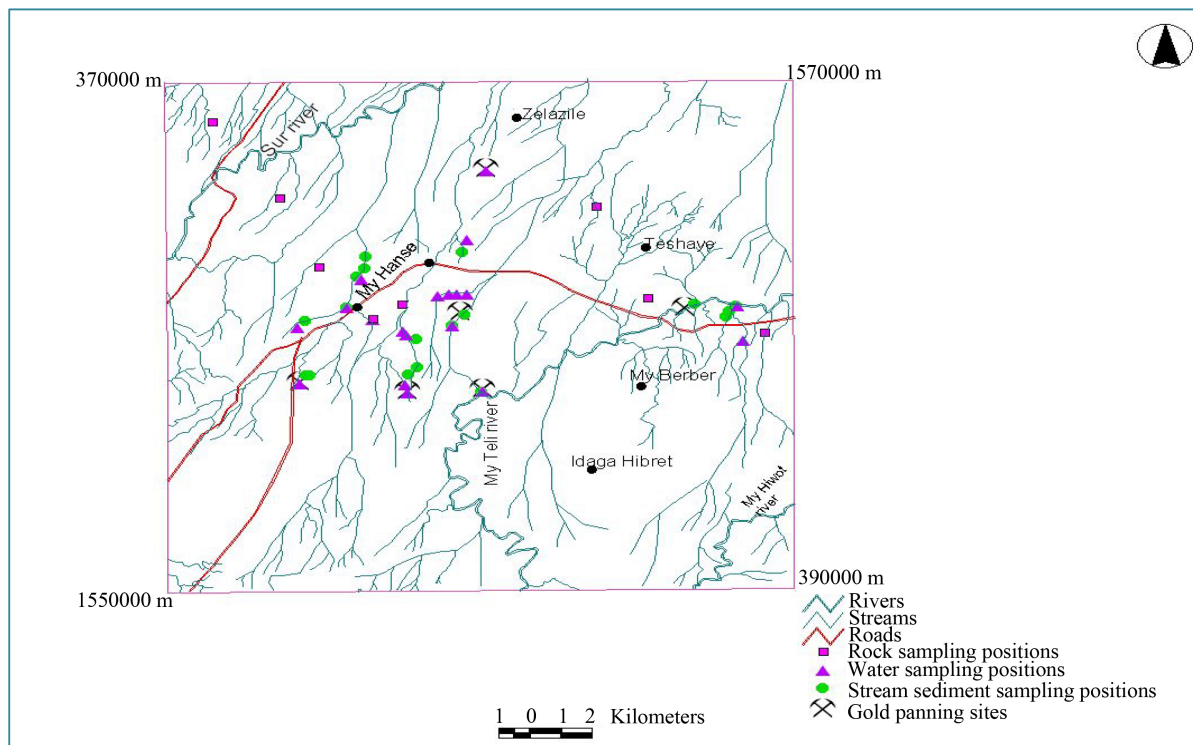

Figure 3. Location map of study area with sample locations and gold panning sites.

bottle was rinsed repeatedly with ground water before taking the samples.

Twenty (20) stream sediment samples were collected from dry and wet stream sediments. Since, some tributaries of seasonal streams have had no water flow for many months: the stream bed was covered by fallen bank materials. The fallen bank material has been removed by digging and the stream sediment was sampled with much care. Most of stream sediment samples were taken from the same site where water sample is collected. About 300 gram the samples were collected using a shovel tool and store in to a clean plastic bags.

Representative rock samples were collected from all mapable units and six of them are selected for thin sec-

tion and XRF analysis. The lithology, structures, mineralization, quartz veins and alteration intensity of the rocks has been studied in the field. A generalized geological map at 1:50,000 scale is prepared based on the satellite image and field data (**Figure 4**).

2.2. Sample Analyses

The chemical analysis of water samples were carried out in the Institute for Applied Geosciences Laboratory at Graz University of Technology, Austria.

Trace elements (Cd, As, Se, Pb, Cr, Ni, Cu, Co V, Sr, Tm, and Ba) were analysed using Inductively Couple Plasma Mass Spectrometer (ICP-MS; Perkin-Elmer Elan 5000) with ultrasonic nebulization and it was calibrated with multi element standard solutions. Acidified samples were used. The detection limit ranges between 0.01 and 0.1 µg/l and precision also reported as 10% for numerous trace elements. Major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were analyzed using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, PERKIN ELMER 4300) and anions (Cl^-, NO_3^- and SO_4^{2-}) were measured using Ion Chromatography (IC; DIONEX 600)/HPLC High performance liquid chromatography.

Rock samples were first crushed in stain less steel jaw crusher and then powdered in an agate meal for chemical analysis and the sample preparation for stream sediments also involves drying in an oven, crushing, grinding, sieving with −200 mesh and packing about 100 mg with plastic bags in Ezana Mining Laboratory, Mekelle. Both rock and stream sediment samples have been sent for trace elements (Cd, As, Se, Pb, Cr, Ni, Cu, Co V, Sr, Tm, Hg, Ba, Zn, Mn, and Mo) and major oxides (SiO_2, Al_2O_3, Fe_2O_3, LOI and MgO) analysis using X-Ray Florescence (PHILIPS PW 2404) spectrometer at the laboratory of Institute for Geoscience, Graz University of Technology, Austria. It was done by two methods-pressed powder pellet for trace elements and fussed glass for major oxides. The samples were initially ground and dried at 110˚C (in fussed glass) and 60˚C (pressed powder pellet) overnight to remove remaining moisture.

2.3. Treatments of Analytical Data

Analytical treatment of data was made in Excel, SPSS, Aquachem and Archview. When analyzing in Aquachem,
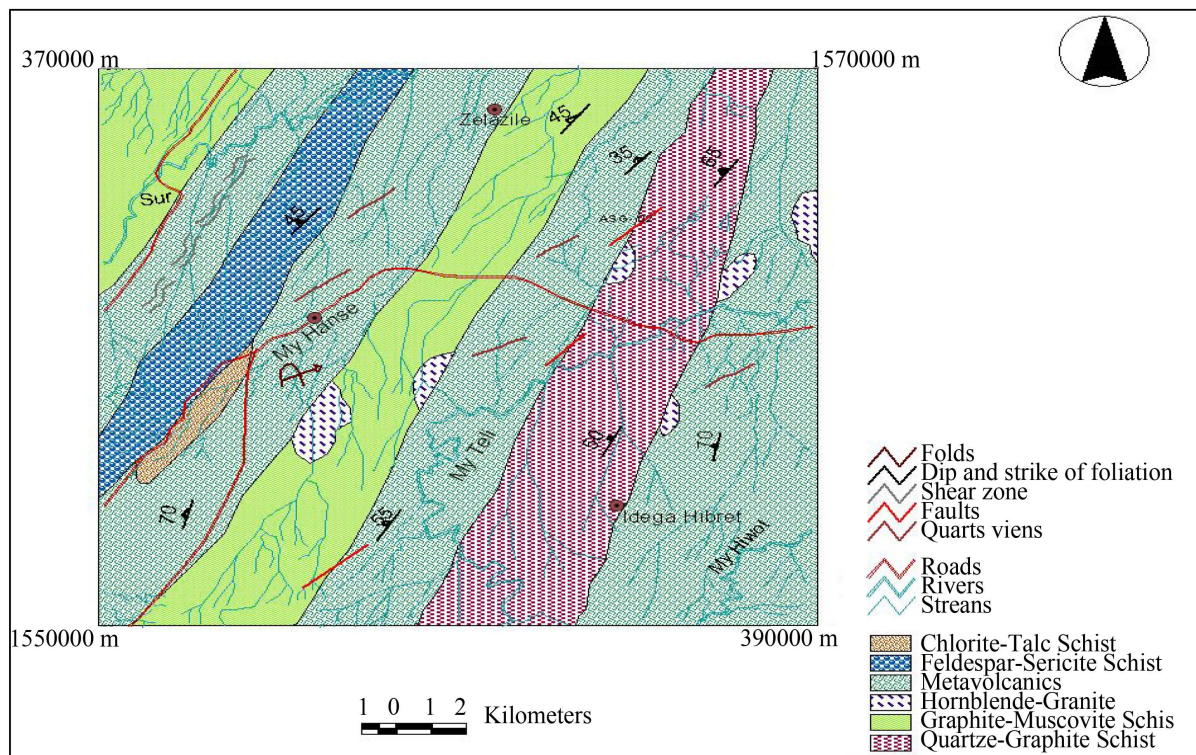

Figure 4. Geological map of Asgede Tsimbla sub catchment area.

SPSS and Archview value below detection limit level where set to zero. Statistical analysis such as mean, median, standard deviation and multivariate analysis (correlation) were used for data analysis.

3. Results

3.1. Lithogeochemistry

Major and trace element analysis of some rock samples obtained from the study area was carried out to find out potential health problems associated with concentrations of particular elements (Table 1).

Table 1. Major (wt %) and trace (ppm) element compositions of selected rock samples in the study area.

Rock Type	Graphite Schist (ATR3)	Graphite-Muscovite-Schist (ATR5)	Feldespar-Sericite Schist (ATR1)	Metavolcanics (ATR2)
Major oxides				
SiO_2	70.39	64.17	64.21	67.27
Al_2O_3	15.11	18.55	15.99	15.58
Fe_2O_3	2.72	5.69	6.85	6.04
LiO	4.96	5.89	2.43	1.57
Na_2O	1.44	1.06	4.43	3.67
MgO	1.15	1.5	1.59	1.84
K_2O	2.62	2.15	1.69	1.27
TiO	6.65	0.69	1.63	0.68
Mn	0.11	0.16	0.08	0.05
P_2O_5	0.02	5.16	0.19	0.2
CaO	0.83	0.1	0.88	1.82
Total	106	105.08	99.97	99.99
Trace elements				
Cu	28	153.1	67.5	14.8
Cr	222.3	147.6	149.5	67.9
Mn	786	1342.8	536.8	708.5
Sr	111.1	34.6	267	162.3
Zr	195	274.1	162.5	157.6
Ba	182.6	1939	384.5	598.8
Rb	73.3	67.2	41.7	37.6
pb	11.7	12.3	9.4	5.5
Ni	17.7	54.7	18.4	9
Zn	51.7	107.2	62.4	71.6
Co	1.3	14.3	10.5	7.9
Cd	4.4	5	5.8	5.3
Hg	bdl	bdl	bdl	bdl
Sb	bdl	bdl	bdl	bdl
Cs	bdl	bdl	bdl	bdl
Ce	29.4	55.1	27.7	29.7
U	3.3	4.1	0.5	0.1
V	193.4	162.7	89.4	88.3

3.2. Hydrogeochemistry

The analytical results and summery statistics (mean, minimum, maximum and standard deviation) of selected elements in water samples from Asgede Tsimbla sub catchment area are presented (**Table 2**). It gives the analytical techniques for different elements/parameters and shows how many orders of magnitude the natural concentration of the analyzed elements cover in this data set. It provides additional information on water standards [6]-[8] and show the percentage of samples above maximum acceptable concentrations (MAC) limits.

3.2.1. Major Ions

The collected surface and ground water samples ware analyzed for Major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and anions (Cl^-, NO_3^- and SO_4^{2-}) and only two major ions (*i.e.* Mg^{2+} and NO_3^-) ware exceeded the quality standards set for drinking water (**Table 2**). In terms of chemical composition (**Appendix B**) generally classifies as: - about 60% of the samples have Mg and the rest has Ca followed by Na as dominating cations; according to anion NO_3 as dominate and Cl followed by SO_4. The water composition can also be arranged as $Mg^{2+} + Ca^{2+} > Na^+ + K^+$ and $SO_4^{2-} + Cl^- > NO_3^- + CO_3^{2-}$.

3.2.2. Trace Elements

Out of 35 trace element analysis the following seven elements show value exceeding the maximum acceptable concentration (MAC) limits (**Table 2**): Br, Al, Fe, F, As, Pb and U (WHO standards).

1) Bromine

The results of bromine ranges from 0.11 - 1.48 mg/l with mean value of 0.67 mg/l. In the study area 1.48 mg/l is maximum in the ground water whereas 0.93 mg/l has to be in the surface water. The highest bromine value (AT-15) (**Appendix B**) is found in the borehole around Mai Lomine Village. All the results are found to be above WHO maximum allowable level—0.01mg/l (**Table 2**). The spatial distribution of fluorine is shown on (**Figure 5**).

Table 2. Range, Mean and standard deviation of the analytical data for selected elements in water samples and their comparison with different water standards.

Parameters	Techniques	Units	Range	Mean	Std. Deviation	Standards (MAC)			>MAC* (%)
						WHO (2004)	Ethiopian (2002)	USEPA (1997)	
As	ICP-MS	µg/l	bdl-23.7	2.47	6.73	10	10	10	10
Pb	ICP-MS	µg/l	bdl-24.6	1.24	5.34	10	20	10	5
Al	ICP-MS	µg/l	bdl-553	73.75	137.76	200	400	50 - 200	30
Fe	ICP-MS	µg/l	bdl-1939	1.49	3.69	300	400	300	20
Cd	ICP-MS	µg/l	bdl-0.21	0.068	0.048	3	3	3	-
Tm	ICP-MS	µg/l	bdl-0.40	0.031	0.068	-	-	2	-
Ni	ICP-MS	µg/l	bdl-0.255	0.04	0.06	20		-	-
Co	ICP-MS	µg/l	bdl-0.56	0.122	0.138	-	-	-	-
Se	ICP-MS	µg/l	bdl-13.99	2.16	3.04	10	10	10	5
U	ICP-MS	µg/l	0.05 - 4.32	0.88	1.10	2	-	-	5
Br	IC	mg/l	0.11 - 1.48	0.67	0.405	0.01	-	0.01	100
F	IC	mg/l	0.21 - 16.5	1.86	4.12	1.5	3.0	4.0	20
NO₃	IC	mg/l	0.01 - 51.8	11.93	1.75	-	50	10	10
SO₄	IC	Mg/l	1.12 - 435	69.5	8.1582E1	500	-	-	-
Mg	ICP-AES	mg/l	7.56 - 127.	59.68	3.3952E1	-	-	-	-
pH			6.11 - 8.3	7.12	0.653	-	6.5 - 8.5	6.5 - 8.5	

Note: ->MAC* (%) = greater than Maximum acceptable concentration for number of samples in percentage.
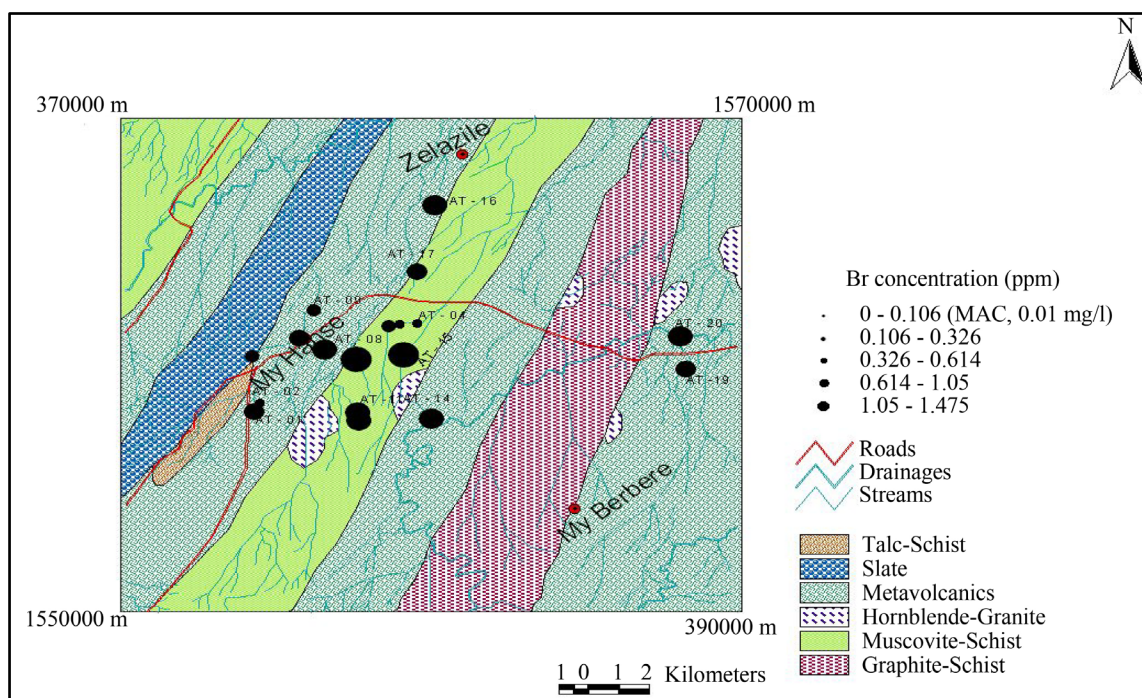
Figure 5. Spatial distribution of bromine concentration in surface and ground waters of Asgeda Tsimbla sub catchment area. Maximum admissible concentration (MAC) is also given in bracket.

2) Fluorine

The surface and ground water collected from various sites of Asgede Tsimbla area contained fluorine of 0.21 - 16.49 mg/l with an average value of 1.18 mg/l (**Table 2**). The maximum value of 16.49 mg/l recorded in sample (AT-16) (**Appendix B**) collected from borehole at Sembel Village, NE of Mai-Hanse Town, while the maximum value of 0.79 mg/l collected from surface water. Four of the samples indicate values higher than Maximum allowable limit (1.5 mg/l) of WHO (2004) drinking water guideline (**Table 3**). The spatial distribution of fluorine is shown on **Figure 6**.

3) Aluminium

The surface and ground water collected from various sites of Asgede Tsimbla area contained Al from less than the detection limit (0.01 ppb) up to 553 ppb, with an average value of 73.75 ppb (**Table 2**). The highest concentration of Al was observed in a sample (AT-07) (**Appendix A**) collected from borehole near Mai Hanse Town while in surface water 155 ppb was observed as a maximum value. 30% of the sample value indicates above MAC (*i.e.* 100 µg/l) based Canadian guideline for drinking water (1996).

4) Arsenic

The concentration of arsenic ranges from less than the detection limit (0.01 µg/l) up to 23.7 µg/l with a mean value of 2.47 µg/l (**Table 1**). 23.7 µg/l is maximum concentration in ground water while 20.2 µg/l in the surface water. The highest values was recorded in samples (AT-10 and AT-11) (**Appendix A**) collected around Fesfesay River, where intensive artisanal gold mining had been taking place and is located south-south east of Mai Hanse Town. Only two samples (10%) fall above MAC of As (10 µg/l) in the study area.

5) Selenium

The value of Se varied from less than detection limit (0.01 ppb)-13.9 ppb with an average value of 2.16 $\mu g \cdot L^{-1}$. In the study area the maximum value in ground and surface water was recorded as13.9 ppb and 4.70 ppb respectively and only one sample (AT-20) exceeds the WHO safe limits (**Appendix A**). The maximum value of 13.9 ppb (AT-20) was observed in a sample collected from Mai-Hammar River, where artisanal gold mining practices had been caring out.

3.3. Stream Sediment Geochemistry

The analytical results and summery statistics value of stream sediments are listed (**Table 3**). It gives additional

Table 3. Analysis results of heavy metals in stream sediments (ppm) and its mean value in comparison with world geochemical background value in average shale.

Sample no.	Zn	Ni	Pb	Cu	Co	Ag	Cr	Mn
ASG-01	70	33	1	42	39	1.4	77.8	539
ASG-02	79	65	9	71	52	1.5	68.9	708.
ASG-03	59	24	5	29	30	1.1	131	359
ASG-04	63	37	5	38	34	1.2	227	451
ASG-05	63	44	4	45	37	1.3	154	1100
ASG-06	71	34	3	45	30	1.2	188	410
ASG-07	105	37	6	44	29	1.2	171	399
ASG-08	66	29	4	32	22	1.9	172	265
ASG-09	33	18	3	20	24	2.0	160	536
ASG-10	64	28	3	30	19	1.76	149	255
ASG-11	76	32	8	38	21	2.2	147.6	354
ASG-12	68	29	8	34	24	2.1	151.2	231
ASG-13	57	26	5	30	20	1.6	143	350
ASG-14	78	36	6	43	25	1.8	128.4	255
ASG-15	50	22	7	29	18	2.3	164.6	354
ASG-16	107	54	12.3	37	19	2.2	132.4	229
ASG-17	84.7	41	11.4	31.6	32	2.4	136.2	260
ASG-18	86	45	13.6	33	37	2.7	147.6	786
ATS-19	26.3	18	16.5	11	48	5.2	251.3	623
ATS-20	48.9	19	6.5	75	54	5.3	160.6	478
Minimum	26.3	18	1	11	18	1.1	68.9	229
Maximum	107	65	16	75	54	5.3	251	1100
Mean	67.7	33.55	6.86	37.8	30	2.1	152.8	447.1
Average shale[a]	95	68	20	45	19	-	90	850

Average shale[a]: world gechemical background value in average shale [9].

information on world geochemical background value in average shale of each element concentration.

4. Discussion

4.1. Lithogeochemistry

The composition of surface waters and shallow ground waters will closely reflect the local geology. Weathering acting on mineral deposits contributes to promote a local rise of the contents of major, minor and trace elements. These anomalous can be identified in soil, stream sediment and waters [10].

In terms of trace and major element analysis the mtavolcanics, Feldespar-Sericite Schist and graphite schist samples are enriched with Mo, Cu, Mn, Cr, and Rb elements and have high SiO_2, Al_2O_3, Fe_2O_3 and LIO as major oxides (**Table 3**). Concentration of these elements vary widely among rock types; so health issue related to water interaction with rocks are different according to the geographic distribution of the rock types.

The chemical transmission of health risk in fact began from rocks with enhanced or reduced contents of elements of greater significant for life [10]. Health issue related to water and stream sediments in the study area are generally derived from the basement rocks upon weathering. Stream waters drained through soil waste disposals from artisanal gold panning sites, which could contain high level of contaminants are supposed to be as a
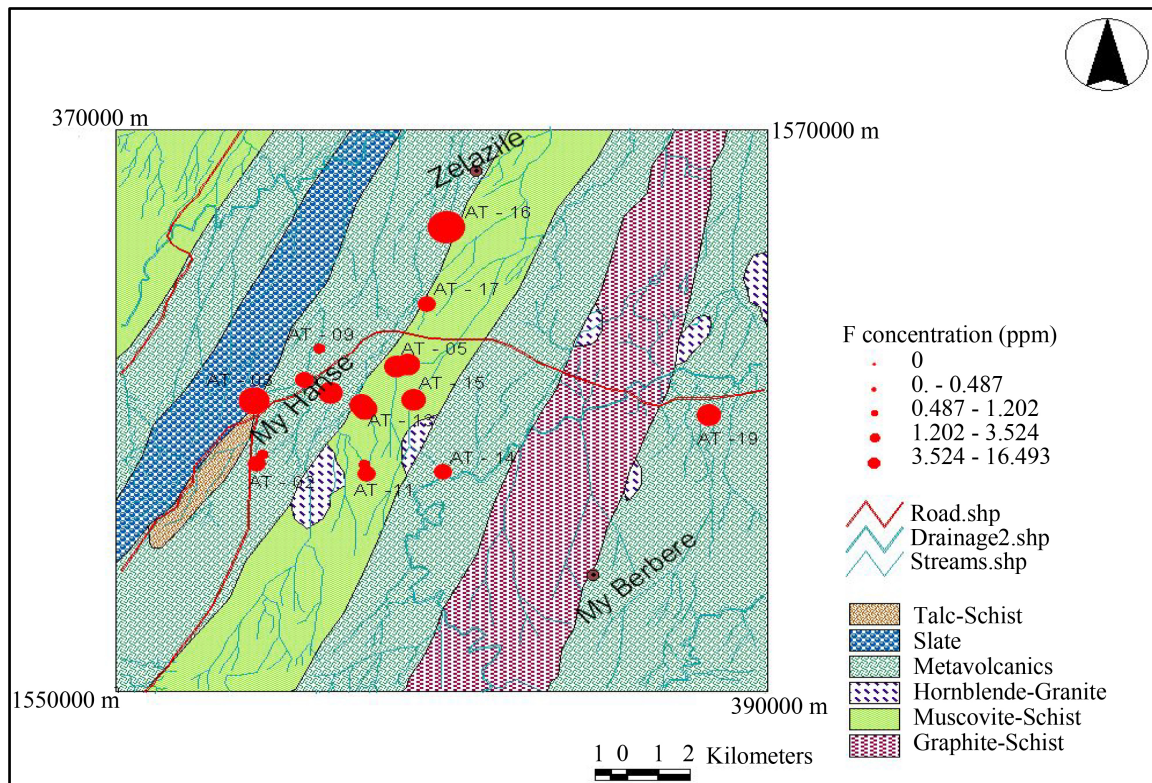
Figure 6. Spatial distribution of fluorine concentration in surface and ground waters of Asgeda Tsimbla sub catchment area.

secondary source of water pollution in the area. Agricultural fertilizers and pestsides released in to the soil might be also considered as important factors in concentration of some trace elements in surface and ground water of the area.

4.2. Hydrogechemistry

The chemical composition of rocks, mineral and soils through which the groundwater flows causes very large variations of the chemistry of the ground water [11]. The ground and surface water in the study area is directly using as drinking water and obviously there is a link between water chemistry and health. The results of elements above MAC and elements which have health impact in its low level such as selenium are presented and discussed as follows. Selected parameters in geochemical environment as a cause of some diseases and their possible source of contaminants are presented (**Appendix C**).

Bromine: Maximum acceptable concentration (MAC) of 0.01 mg/l for bromine in drinking water has been established on the base of health consideration. All the results are found to be above WHO maximum allowable level—0.01 mg/l (**Table 2**). The values of Br could be related to the use of fertilize and pestsides in agriculture and artisanal gold mining practice.

The bromine concentration in rocks, soils and freshwater usually are very small. The values of bromine in the study area could probably as bromine from mining, fertilizer and pesticides release into soil; in turn bromine leached from soils when they flooded into surface and ground water.

Some of health effects that can be caused by excess bromine value in water are malfunction of nervous system, gastrointestinal and disturbances in genetic material; and also cause damage to organs such as liver, kidneys, lungs, thyroid glands. Some forms of organic bromine, such as ethylene bromine, can even cause cancer [8].

Fluorine: The World Health Organisation (WHO) guideline value for fluorine in drinking water is 1.5 mg/l, but in most samples about (55.5%) of the fluoride contents were above the 0.5 mg/l, the limit recommended for tropical countries by WHO [10]. Some other researchers have been suggested 0.7 mg/l as an action level for

tropical countries with high daily intake of water [8]-[10] have also been noted the WHO recommended levels of 1.5 mg/l fluorine in drinking waters are not acceptable for hot and dry climate.

Fluoride enrichment in the surface and ground water could be related to leaching of rocks rich in fluorine such as granite (*i.e.* as granite sample in the study area constitute fluorine bearing minerals such as biotite, hornblende and sphene) and muscovite-schist, where this rock unit also contains muscovite, biotite and feldspar minerals which are considered as fluorine rich minerals. Rock-water and soil-water interaction; weathering and leaching of fluorine bearing rocks and minerals could be considered as important factors in the concentration of fluoride in the surface and ground water.

Excessive intake of fluoride rich- water can cause dental fluorosis (mottling of teeth), skeletal fluorosis (depilating disease, which affect bones) and harm nerves and muscles. The high fluoride is not only possible risk factor but it is possible that there is some relationship with the disease or it could even increase the severity of the disease [1]. Many animal experiments reported that the kidney damage can occur even at low levels of fluoride exposure over large period of time [12].

Aluminium: The study area show maximum level in ground water to be 553 ppb. As Al is found in most rocks abundantly, the values could be related to natural sources (*i.e.* rocks, soils and their derivative minerals) and to some extent anthropogenic activities such as artisanal gold mining and agriculture. Al in the surface and ground water could be derived from weathering of rocks rich in Al and leaching of soils accumulated from such activities as artisanal gold mining and agriculture.

Aluminium is included in the priority list of hazardous substance identified by agency for toxic substance and disease register (ATSDR). Sign and symptoms of aluminium toxicity include colic, dementia, esophagitis, gastroenteritis, kidney damage and liver damage [8].

Arsenic: The high amount of arsenic value in water of Asgede area could be introduced through anthropogenic activities (*i.e.* artisanal gold mining) and the dissolution of arsenic containing bed rock (Phylite/Slate) and minerals such as pyrite and chalcopyrite.

Ingesting inorganic arsenic contaminated drinking water cause skin cancer, tumours of the bladder, kidney, liver (the primary carcinogen) and lungs. High level of in organic arsenic in food or water can be fatal, a high level 60 parts per million parts of food or water (60 ppm) [8]. Adverse health effects of too high arsenic value in drinking waters have recently received much attention [13].

Selenium: The selenium concentration in waters are generally very low and only rarely exceeds the WHO safely limits of 10 µg/l [14]. The study area show about 40% of the sample analysed was <1 µg/l and only one sample (AT-20) exceeds the WHO safe limits and this could be related to artisanal gold mining practise in that river.

Concentration of selenium in fresh water around the world is 0.2 µg/L [15], in Asgede Tsimbla area selenium concentration in some well waters observed as low as 0.01 µg/L.

Selenium appears to be essential element in human nutrition. It is part of the biological important enzyme glutathione peroxydase (PHS-PX) which acts as antioxidant preventing tissue degeneration. Selenium prevents the toxicity of several other metals such as silver, mercury, cadmium and lead. Selenium, at trace levels is essential in human and animal diet and its deficiency has received much attention. It causes symptoms such as muscular degeneration, impeded growth, fertility disorders, anemia and liver disease [16]. Keshan and Kaschin-Beck disease reported on regional scale from China, are caused by Se deficiency. The recommended daily intake described by many researchers and agencies for Se is about 35 µg per day and doses larger than 200 µg can be toxic [17]. Other researchers e.g. Fordyce *et al*. [14]; Yang and Xia [18] had noticed deficiency level (<11 µg/g per day) and toxic level (>900 µg/g per day) for selenium. Anyway Se is an element that should better have a minimum guideline level by WHO.

Iron and magnesium falls above MAC, but there is no evidence of adverse health effects specifically attribute to these elements in drinking water, and are more aesthetic nature (cause undesirable test and odor to the water) or limit the use of water for practical purpose.

Bivariate Correlations

Cu and Se show similarity in distribution pattern and have positive correlation. The trend between Cu and Se could origin from dissolution of sulfide minerals. The similar behavior of Cu and Se can be explained by their geochemical similarity, which are Chalcophile elements (prefer to bond with sulfur). The trend between Al and Fe also indicate strong positive correlation. This could be interpreted as indicative of common source for them.

Table 4. US EPA guidelines for sediment quality as compared to present study-Asgeda area.

Metal	Not polluted	Moderately polluted	Heavily polluted	Present study
Ag	-	-	-	1.1 - 5.3
Cu	<25	25 - 50	>50	11 - 75
Ni	<20	20 - 50	>50	18 - 65
Pb	<40	40 - 60	>60	1.1 - 5.3
Co	-	-	-	18 - 54
Cr	<25	25 - 75	>75	68.9 - 251
Mn	<300	300 - 500	>500	229 - 1100

Fluorine show negative correlation with bromine and this could indicate that they have different origin.

4.3. Stream Sediment Geochemistry

The accumulation of heavy metals in sediments can be a secondary source of water pollution, once environmental condition is changed [19]. There for an assessment of heavy metal contamination in sediment is an important tool to assess the risk of hydrogeochemical environment. Assessments of metal contaminants in the area are discussed bellow.

Assessment According to United State Environmental Protection Agency (US EPA)

The chemical contamination in sediments was evaluating by comparison with sediment quality guideline proposed by US EPA. These criteria are shown (**Table 4**). Pb in all stations under investigation was belong to unpolluted sediments, while elements Cu, Ni and Mn are considered as moderately polluted and Cr more or less belong to heavily polluted.

5. Conclusions

The ground and surface water in some zones of the study area has values of Br, F, Al, As, Pb, U, Fe, Mg and NO_3 exceeding MAC guideline standards for water. Br and F account for almost all the elevated values. The association of F, Br and Cl is found as geochemical indicator of liver cancer in areas such as Parana-Brazil, China and Srilanka [20].

Trace elements like Cd, Cr, pb, Be, and Tm which have serious health effects fall to pass quality standards set for drinking water. Only two sample sites fall above MAC for As and these may not considered as a major problem in the area. From present study the water quality is therefore better than expected. The ground water is generally weak acidic to basic and the dominate ions are Mg and NO_3.

It is clear that health relates not only to excesses of trace elements in drinking water supplies, but may also relate to deficiencies (e.g. Se). The majority of water and stream sediment samples of analyzed results in the study area show significantly low as compared to worldwide values of Se for these geochemical medias.

The accumulation of heavy metals in sediments can be a secondary source of water pollution once environmental condition is changed [19]. The Geo-Accumulation Indexes (Igeo) of some heavy metals such as chromium, cobalt, copper, and lead are calculated for stream sediment quality in the study area and give values from unpolluted to moderately polluted.

Although liver related disease has been identified around shire area, the causes of the disease remain unclear. Environmental factors are mostly considered to explain the etiology of this liver related disease.

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Appendices

Appendix A. Trace element chemical analysis of water samples.

No	Al (µg/l)	As (µg/l)	Pb (µg/l)	Fe (µg/l)	Cd (µg/l)	Tm (µg/l)	Ni (µg/l)	Co (µg/l)	Se (µg/l)	U (µg/l)	B (µg/l)
1	<0.01	<0.01	<0.01	10	0.087	0.021	<0.01	0.321	0.53	0.066	4.0
2	2.5	2.8	0.21	78	0.029	0.023	<0.01	0.098	2.13	0.106	44.3
3	<0.01	<0.01	<0.01	306	0.158	0.022	0.015	0.245	<0.01	1.288	7.5
4	2.5	2.8	0.21	78	0.207	0.021	<0.01	0.209	0.96	0.702	10.7
5	<0.01	<0.01	<0.01	<0.01	0.168	0.029	<0.01	0.255	<0.01	4.363	10.9
6	<0.01	<0.01	<0.01	1939	0.150	0.026	0.097	0.558	<0.01	0.050	14.7
7	553	<0.01	24.16	370	0.121	0.026	<0.01	0.178	<0.01	1.318	9.0
8	127	<0.01	<0.01	99	0.083	0.022	0.025	0.182	4.26	0.173	165.3
9	155	<0.01	<0.01	16	0.091	0.021	0.012	0.171	3.36	0.349	117.2
10	36	23.7	<0.01	37	0.080	0.032	0.255	0.123	4.06	0.633	23.0
11	<0.01	20.2	<0.01	383	0.078	0.021	0.156	0.125	<0.01	1.321	14.5
12	313	<0.01	<0.01	<0.01	0.089	0.021	0.114	0.227	3.34	0.433	18.1
13	<0.01	<0.01	<0.01	26	0.077	0.022	<0.01	0.237	4.37	0.765	54.2
14	3	<0.01	<0.01	197	0.087	0.027	<0.01	0.273	3.48	1.885	<0.01
15	113	<0.01	<0.01	20	0.105	0.025	0.003	0.160	0.21	0.071	17.9
16	<0.01	<0.01	<0.01	990	0.073	0.023	<0.01	0.406	4.60	0.144	55.3
17	42	<0.01	<0.01	77	0.092	0.020	<0.01	0.178	4.70	1.056	50.7
18	46	<0.01	<0.01	27	0.068	0.020	0.027	0.296	4.70	1.975	<0.01
19	17	<0.01	<0.07	5	0.101	0.021	0.011	0.249	6.85	0.507	19.0
20	<0.01	<0.01	<0.01		0.101	0.021	<0.01	0.249	13.99	0.507	19.0

No	Ba (µg/l)	Be (µg/l)	Ce (µg/l)	Cs (µg/l)	Sm (µg/l)	Rb (µg/l)	Sr (µg/l)	Ag (µg/l)	Cu (µg/l)	Zn (µg/l)
1	44	0.051	0.034	0.27	0.026	0.89	4338	<0.01	0.41	13.53
2	23	0.027	0.033	0.21	0.027	0.85	115	<0.01	0.85	4.84
3	167	0.031	0.192	1.60	0.050	1.06	1434	<0.01	0.21	1.31
4	68	0.024	0.029	2.60	0.022	0.17	1597	<0.01	0.36	11.78
5	67	0.076	1.660	1.93	0.212	1.23	1488	0.27	0.97	11.94
6	56	0.044	0.274	1.32	0.060	2.23	292	<0.01	0.22	5.33
7	83	0.043	0.742	1.16	0.107	0.30	524	<0.01	0.69	1.24
8	118	0.027	0.245	0.87	0.046	4.86	302	<0.01	0.96	2.88
9	68	0.022	0.068	0.60	0.030	1.26	307	<0.01	0.54	0.24
10	14	0.039	1.953	0.54	0.295	0.49	87	<0.01	1.70	0.52
11	59	0.023	0.010	2.80	0.023	0.59	420	<0.01	0.66	<0.01
12	97	0.024	0.123	1.03	0.039	1.23	527	<0.01	1.55	<0.01
13	82	0.027	0.148	1.06	0.047	1.11	503	1.69	1.35	6.10
14	77	0.026	0.079	1.48	0.043	0.88	716	<0.01	0.99	<0.01
15	10	0.026	0.120	1.23	0.040	0.52	178	<0.01	0.07	<0.01
16	73	0.027	0.261	0.82	0.050	0.92	444	<0.01	0.75	6.03
17	40	0.021	0.064	0.85	0.029	0.68	601	<0.01	0.86	1.77
18	81	0.020	0.051	1.59	0.028	0.55	843	<0.01	0.65	<0.01
19	105	0.021	0.206	0.80	0.049	0.97	703	0.35	1.58	3.39
20	81	0.021	0.206	0.80	0.043	0.49	87	0.30	1.35	0.52

Appendix B. Major ions chemical analysis and water type.

Sample No	F	Br	NO₃	SO₄	HCO₃	K	Na	Ca	Mg	Water type
AT-01	0.3737	0.4743	0.3595	435.3391	299.8	1.3154	23.1404	252.8269	7.5592	Ca-SO₄-Cl-HNO₃
AT-03	0.01	0.883	51.3786	13.3591	278.75	3.9794	7.5569	29.6082	93.5829	Mg-HNO₃-Cl
AT-05	0.6964	0.1067	24.5498	22.7953	872.00	2.3244	77.1731	112.5096	30.9147	Sr-Na-HCO₃
AT-06	1.0424	0.2695	8.8919	46.0297	616.00	2.664	128.897	90.3463	47.5582	Ca-Na-Mg-HCO₃
AT-07	3.5244	0.4623	0.198	182.4118	740.18	3.5602	166.7217	60.4901	41.0573	Na- HCO₃-Cl-SO₄
AT-08	0.2506	0.2031	0.0069	58.8343	538.34	8.3995	24.2788	36.4384	16.9719	Ca-Mg-Na- HCO₃-Cl-SO₄
AT-09	0.7904	0.3267	1.0275	150.7578	116.32	3.2922	75.1462	42.7848	20.1805	Na-Ca- HCO₃-Cl-SO₄
AT-10	0.01	0.9031	34.5338	16.3117	191.96	4.7115	13.3544	36.8005	126.7885	Mg-Ca
AT-11	0.3396	0.9303	18.7139	21.5874	0.17	5.5722	35.1257	45.7797	103.3873	Mg-Ca-Na
AT-12	0.01	1.3663	0.5617	159.1126	55.63	1.4776	112.6191	8.8124	87.104	Mg-Na-HCO₃-Cl
AT-13	0.747	0.2089	1.6022	45.8517	718.71	4.0057	49.7108	39.4576	28.872	Mg-Na-Ca-Cl-HCO₃
AT-14	0.7309	0.9971	0.4488	226.5273	260.06	3.2033	78.7514	97.5354	54.7073	Ca-Na-SO₄-HCO₃-Cl
AT-15	0.4872	1.4755	2.4962	116.0967	263.07	2.2248	60.328	58.4001	75.0533	Mg-Ca-Na-HCO₃-Cl-SO₄
AT-16	1.2021	0.941	14.6134	145.5691	261.66	5.984	108.8469	106.7415	53.5304	Ca-Na-Mg-HCO₃-Cl
AT-17	16.4932	0.506	0.2541	1.1178	681.86	1.5381	47.1395	11.0219	68.832	Mg-Cl-HCO₃
AT-18	0.3493	0.6147	1.6146	105.3168	335.43	4.5565	52.6247	43.4327	91.0991	Mg-Cl-HCO₃
AT-19	0.3512	0.5082	1.7603	104.8366	316.93	4.5399	52.5605	43.365	91.0324	Mg-Na-Cl
AT-20	0.6599	1.0503	51.752	140.3853	62.12	1.8192	134.5995	110.9888	36.0528	Na-ca-Cl-HCO₃
					648.16					

Appendix C. The occurrence of some disease and their possible contaminants. Selected parameters in geochemical environment (surface and groundwater) on the occurrence of some diseases and their possible source of contaminants.

Parameters	MAC (μg/l), WHO, EU and Canadian	Potential health effects		Source of contaminants
		Deficiency	Abundance	
As	10	-Insufficient hair growth -Spleen enlargement	-Skin cancer -Tumours of bladder, kidney, liver and lungs.	-Natural deposit, electronic waste.
Pb	10		-Kidney, liver, heart and nervous system damage.	-Natural and industrial deposits.
Se	10	-Breast, gastrointestinal and skin cancer. -Liver damage and heart muscle disorder	-Hair and nail loss -Nervous disorder	-Natural deposit, mining, smelting and coal combustion
Tm	10		-Kidney, liver, brain and intestinal effects	-Electronic, drug and alloy
Br	10		-Malfunctioning of nervous system -Liver, kidney, lung and thyroid gland damage.	-Natural deposit
Cr	50	-Diabetes	-Liver, kidney and circulatory system disorders -Lung cancer	-Natural deposit, mining electroplating.
Cu	1000	-Anemia	-Gastrointestinal irritation	-Natural/industrial deposit, wood preservation
Al	100		-Kidney and liver damage -Dementia, colic and esophagitis	-Natural/industrial deposits

Continued

F	1500	-Developmental defects of bone and teeth	-Dental and skeletal flourosis	-Natural deposits
NO$_3$	45,000		-Metamoglobulinemia	-Animal waste, fertilizer and natural deposit
Cd	10	-Growth reduction	-Kidney effects -Cancer of prostate	-Natural deposit -Galvanized pipe corrosion