

**Master Thesis, Department of Geosciences**

**Hydrogeochemical and trace element  
contamination investigation, Northern  
Ethiopia, Asgeda Tsimbla Sub catchment area,  
And its implications to recent chronic liver disease**

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Master Thesis in Geosciences

Discipline: Environmental Geology and Geohazards

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**October 01 2013**

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This work is published digitally through DUO – Digitale Utgivelser ved UiO

<http://www.duo.uio.no>

It is also catalogued in BIBSYS (<http://www.bibsys.no/english>)

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## **Acknowledgements**

I would like to thank the Norway Quota Scheme scholarship program for giving me this opportunity to study at university of Oslo. I would like to thank all who has helped me throughout this study. First of all I would like to thank my advisors Professor Per Aagaard for giving me opportunity and for his support, advice and contributions. I would also like to thanks the following persons: the technical staff at the department of Geosciences, University of Oslo; Mufak Naoroz, a person who did a great job in the lab analysis and Maatern Aerts for the XRD analysis. And I especially thankful to my numerous friends who did helped me along this whole study.

Back home, I would like to express my special thanks for my parents providing loving encouragements for me during my stay in Oslo.

## **Abstract**

Chronic liver disease is recently becomes the most sever disease to residents of northern Ethiopia (Shire area) which was started 1980. Pervious health study reviles that this liver disease is not caused by virus and there is a fear that it can be caused by toxic chemical pollutants from the water they used to drink. Therefor the main objective of this study is to identify which geochemical elements cause this disease and its associations, to map their spatial distribution and lithological associations, to see how using compositional data analysis improves analyzing association within geochemical elements as compared to normal (classical) statistical method and to simulate how nitrate and carbon from the recent fertilizer practice can change the dissolution rate of trace elements by changing redox system of aquifers. During filed work 16 water 16 soil and 14 rock samples were collected. Chemical analysis of trace elements was done by Inductively Couple Plasma Mass Spectrometer (ICP-MS) for water and Optical Emission Spectrometry (ICP/OES) for soil and rock samples. Statistical analysis was done by different software's like excel, past, R, CoDaPack and PHREEQC for redox reaction simulation. The analysis reveals that the potable quality of water is poor and the possible cause of this disease could be Pb and Zn at the eastern and As at the western part of the study area and also it could be caused by the interaction of elements of additive or synergetic effects. The high value of; TDS, pH, sulfate, association of Cu, Fe, Mo and Mn with Pb and Zn in water samples and high sulfur and Polar organic compounds in the rock samples indicates that the incidence of liver disease at eastern part of the study area is related to graphite schist type of rock which could be related to the organic sulfide minerals. There is lack of pattern in association of trace elements within water, soil and rock samples which could be because of the dispersion process and the high transmissivty of highly fractured aquifers found in the study area. Compositional data analysis does not improve the relationship analysis between geochemical pollutants. This could be because of in compositional data analysis data are transformed in logratio which is a logarithmic function. This logarithmic and ratio function removes the influence of anomalous values which are the crucial values that cause different biotoxic effect to human health. The reason for the recent occurrence of this liver disease could be related to the recent fertilizer practice. The simulation indicates that nitrate and carbon could change the dissolution of trace elements from sulfide minerals in the anoxic zone of aquifer system by change the redox system of a given aquifer. Trace element pollution study is a complex science it needs a lot of investigation.

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# 1 Introduction

One of the major prerequisites for a healthy life is an adequate supply of safe drinking water, but waterborne related diseases are still a major cause of death in many parts of the world especially in developing countries (WHO, 2011, Selinus, 2005). All water contains both natural contaminants, particularly inorganic contaminants that arise from the geological formations through which the water flows and, to a varying extent, anthropogenic pollution by both microorganisms and chemicals (Fawell and Nieuwenhuijsen, 2003).

The main inorganic contaminants concern in drinking water are trace elements (García-Lorenzo et al., 2012) which are chemical elements at which the concentrations are less than 1000 ppm or 0.1% of a total rock's composition. Different disciplines use different meanings for the term trace elements in different literatures. For earth scientists trace elements are elements rather than the abundant rock forming elements (O Si Al Fe Ca Na K and Mg). They are those elements that are not stoichiometric constituents of phases in the system of interest (White, 2013). They are important for many critical biochemical processes in living organisms (Bahadir and Duca, 2009) for the proper growth, development, and physiology of the organisms. Trace elements needed in very minute quantities (Selinus, 2005) but the biotoxic effects of many of them in human biochemistry are of great concern.

Historically, the study of trace metal toxicology largely concerned with acute or overt effects (Selinus, 2005, WHO, 2011, Klaassen, 2007). There is, however, growing interest in the study of, subtle, chronic, or long-term effects in which cause-and-effect relationships are not much obvious or may be subclinical. There are a number of diseases proved to be connected to geochemical characteristics of the environment. Studies of relations between geochemistry and human health are very complex and it is a subject of many investigations (Klaassen, 2007, Selinus, 2005), (Appelo and Postma, 2005).

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. So knowledge of rock types and mineralization in a particular area can help to find out potential health problem with concen-

tration of particular elements and the type of trace metal contaminants varies with the mineralization of the area (Pyenson, 2002, Williamson and Rimstidt, 1994).

## **1.1 Background**

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 chronic liver diseases. Chronic liver disease is a disease, which was preceded by mild symptoms of fever, weakness, and jaundice for about a year and may lead to death if not medicated. According to local health office, liver related diseases started in 1980, but recently it becomes the most severe disease in this area and about 270 people and more have died since then. Males and females have been equally affected and children aged between 7 and 15 appear to be most susceptible. By now the rate of disease is elevated and many of the local people have been worrying about the spreading of this liver related disease (Kleiman et al., 2008). The recent study by the ministry of health shows that this liver disease is not transmitted from one person to another person and is not caused by virus and the final cause of this outbreak has yet to be determined. There is a fear that it can be caused by toxic chemical pollutants. Since in the study area there are no industries that can pollute the area, it might source from geochemical pollutants related to the geology of the area.

In the study area there are abandoned artisan placer gold mining sites and many of the individuals have been panning for gold using manual operations for a long time. There are many intermittent streams (most of them used as a source of drinking water) 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. This study seeks to provide answers to some questions cause of this disease either from water they use, soil or stream sediment they use to pan and recommend directions for the future. If this recent outbreak of liver diseases is caused by geochemical trace metal contamination of the ground water that they used to drink, then the main question is why it was not a problem before and why it outbreaks in the recent years? That means there should be recent anthropogenic activities like fertilizer and hand dug well (used for drinking water and irrigation) practice that could

change the chemical environment of ground water and that could lead to dissolution of these contaminants

## **1.2 Objective of the study**

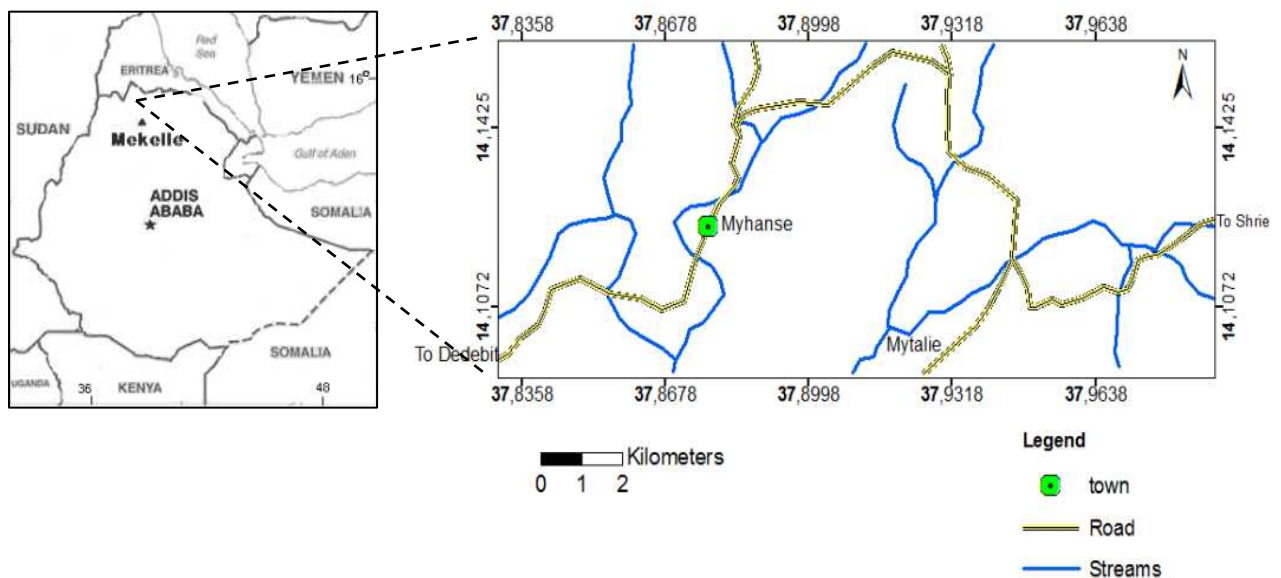
- To assess the potable quality of ground water and to relate with the geological characteristic of the area
- To identify which geochemical elements cause this disease and to map their spatial distribution in the study area
- To map and identify the association of geochemical pollutants and with lithology of the area
- To identify and model the relationship between different multi-variant geochemical pollutants
- To see how using compositional data analysis improves analyzing association between geochemical elements as compared to normal (classical) statistical method in this type of study.
- To simulate how nitrate and carbon can change the redox system of aquifers by a reaction with sulfide minerals, which contain unwanted trace metals that can causes liver disease, using successive incremental reactions



## 2. Study area

### 2.1 Location and Accessibility

The study area is located about 355 km North West of Mekelle, Tigray national state, Northern Ethiopia. Geographically it is located between 1558400 – 1567700m north latitudes and 373650 – 391052m east longitudes (fig 1). Access with in the study area is possible through weathered road connecting to Shire.



**Figure 1** Location map of study area which is part of the Asgede Tsimbla catchement.

### 2.2 Climate

The study area is characterized as semiarid to arid climatic regions. The average annual temperature for the region in generally varies from 24 - 29°C. Records obtained show temperature maxima of between 37 and 40°C and minima of 15 to 19°C. November and December are the coldest months. There are two rainy periods: June – September with highest seasonal rain fall being 500mm and the lowest seasonal rain fall in autumn middle February to April is about 25mm. (National Meteorological Service Agency of Ethiopia, 2008).

## **2.3 Human Settlement**

In general, the area is scarcely populated and population density varies from place to place. Myhanse is a small town around the center of the study area with population of 2575. Most of settlements are three to five households of farmers settle together here and there according to the proximity to their farm lands. The nearest populated town and villages are: - Ddebit (17km south west of Myhanse town with a population of 4787), Adimohameday (18km south-south west of Myhanse with a population of 6302), Kisadgaba (26km north east of the town with a population of 6667), and Hitsats village (15km south east of Myhanse town with a population of 5387)( source from unpublished census report)

## **2.4 Fauna and Flora**

### **2.5 2.4.1 Fauna**

The fauna of Asgede Tsimbla area is represented wild animals such as Jaguar, Jackal, Tiger and Hyena. The other animals which are found in this area include: - baboons, reptiles and other numerous bird species (interview from local people).

### **2.4.2 Flora**

The main plant species known to exist in the area include scattered coniferous, sparse shrubs, Okatrees, and Deciduous trees such as Acacia and Incense.

## **2.5 Physiography**

The area is generally characterized by rugged topography in its southern and western parts. It has an overall tilt of northeast to south west, which has been a controlling factor in the formation of the main drainage system of the area. Metavolcanic and Metagranite generally occupy the high ground while the Metasediment rocks predominantly in the river valleys. The altitude ranges from 1015 to 1145 meters above sea level. Streams are intermittent and often drain northwest direction. The drainage pattern is sub dendritic to well-developed dendritics and the main stream in the study area is called it Myteli.

## **2.6 Land use**

In the study area the majority of the people living in the rural area subsist on mixed farming , they cultivate Wheat, Barley, Sorgem, “Dagusa” and recently “Selite” beside raising Cattle, Goat, Sheep, Donkey and other domestic animals in small number. Artisanal gold mining which is also being carried out intensively in different parts of the study area is another source of their income besides with farming.

## **3. Literature review**

### **3.1 Occurrence of trace elements in the lithosphere**

Geological formations provide major, minor and trace elements to the biological system (Klaassen, 2007). Concentrations of many trace elements varies much larger than variations in the concentrations of major components, often by many orders of magnitude(White, 2013). The concentration of trace elements in soil and ground water are highly controlled by geological processes(Fowler et al., 2011) (Selinus, 2005). In rocks, they exist as their ores in different chemical forms. Trace elements are mainly concentrated in mineralized provinces associated with ore grade rocks(White, 2013, Selinus, 2005). Geochemical provinces are part of earth crust in which chemical composition is significantly different from the average earth crust. Ore grades, which are characterized by mineral deposits, exceed average crystal abundance level by two or four orders of magnitude. Ores can be sulphides, (such as iron, arsenic, lead, lead-zinc, cobalt, gold, silver and nickel sulphides) or oxides (such as aluminum, manganese, gold, selenium and antimony). Some elements can occur as both sulphide and also as oxide ores such as iron, copper and cobalt(Duruibe et al., 2007, White, 2013) and some appear as single element within sulfide or oxide ores(White, 2013). Ore minerals are mostly tend to occur in families, whereby trace elements that exist naturally as sulphides or oxides would mostly occur together (for example sulphides of lead, cadmium, arsenic and mercury would naturally be found occurring together with sulphides of iron (pyrite,  $\text{FeS}_2$ ) and copper (chalcopyrite,  $\text{CuFeS}_2$ ) as minors)(Selinus, 2005).

Organic compounds can sequester and adsorb trace elements and form metallo-organic compounds(Selinus, 2005). In the geological context, organic matter is only preserved in rocks under anoxic conditions, which due to the prevalent redox conditions are also sulfur-reducing

environments that lead to the presence of sulfides. This is particularly important in the formation of rocks described as black shales that become enriched in many trace elements.

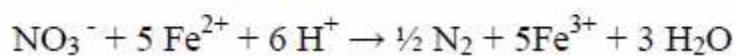
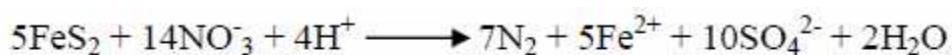
### **3.2 Hydrogeochemical environment and trace element mobilization**

Concentrations of trace elements are usually extremely small in groundwater. They are mostly associated with igneous and metamorphic rocks, and in particular, with ore bodies (Edwards et al., 2000). Weathering of these rocks, including oxidation and leaching, may give rise to elevated trace metal levels in groundwater. Differences in the chemical quality of water from one place to another in an area may reflect differences in the mineral composition of the aquifer (Duruibe et al., 2007), which are signature of the composition of geology of the given area and also depends on the nature of precipitation, climate, biological and anthropogenic activities (Appelo and Postma, 2005). This difference in composition is controlled by two natural (Geologic and biological) and anthropogenic cycles. Geological cycle plays a major redistributing factor of trace elements (Selinus, 2005, Haaijer and Lamers, 2007).

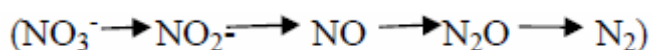
The existence of geologic structures, such as faults, plays a significant role in the transport of geochemical elements. Fracturing is the major factor controlling regional transmissivity variation, it can define the overall geometry of regional flow system by creating large scale flow conduits and also can influence regional ground water chemistry variations (Mayer and Sharp, 1998). The biological cycles also controls the circulation of geochemical elements which include bioconcentration by plants and animals and incorporation into food cycles. Trace metals can be emitted into the environment by both natural and anthropogenic causes; for example; rainwater dissolves rocks and ores and physically transports material to ground water aquifer systems, streams and rivers. Human industrial activity can greatly shorten the residence time of metals in ore and it greatly enhance worldwide distribution not only by discharge to land, water and also to the atmosphere (Haaijer and Lamers, 2007, García-Lorenzo et al., 2012). In some process the mobilization of chemical elements in natural cycles may exceed the anthropogenic cycle (Selinus, 2005).

Based on the water's content of redox-sensitive elements like oxygen, nitrate, iron, sulphate and methane, the ground water system classify into four basic water classes ranging from the most oxidized to the most reduced: Oxygen zone, Nitrate zone, Iron sulphate zone and Me-

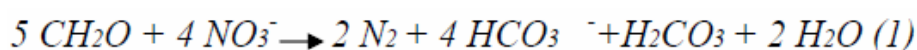
thane zone, from surface to depth (Appelo and Postma, 2005). The Oxygen zone contains considerable amounts of oxygen. The Nitrate zone characterized by its nitrate content but has little or no oxygen. A continuing supply of nitrate will push the redoxcline condition of ground water along the direction of the groundwater flow. The oxidized chemical conditions may reach the aquifer by reduction of nitrate which lead to a high sulphate content in the nitrate zone which is a sign of possible nitrate reduction with pyrite in the sediment, as this reaction among other things produces sulphate. The Iron-sulphate zone is a moderately reduced condition with little or no nitrate, oxygen and methane. The Methane zone is a strongly reduced chemical environment where methane occurs. Nitrate reduction utilizing pyrite as an electron donor is thermodynamically feasible and may be bacterially mediated (Haaijer and Lamers, 2007). When ore rocks like pyrite (FeS<sub>2</sub>) and other sulphide minerals in aquifer exposed to air, in the presence of oxidizing bacteria, such as *Thiobacillus ferrooxidans*, it become oxidised to produce metal ions, sulphate and acidity. This means the equilibrium condition of groundwater composition is mainly controlled through weathering, ionic-exchange, redox reaction and other activities (Appelo and Postma, 2005). These redox conditions might affect by anthropological activities; like using fertilizer can increase the nitrate composition of ground water which might change the redox condition of the given aquifer environment. This process could change the concentration of trace elements in the groundwater system. The oxidation of sulfide mineral especially in crystalline rocks is the major source of trace element contamination in ground water aquifer systems. For example in reducing environment pyrite could oxidize by anthropogenic addition of nitrate in the aquifer system as follows (Williamson and Rimstidt, 1994);



The oxidation of pyrite is reflected by increase in sulfate and Fe<sup>2+</sup>. The presence of organic matter can also affect the redox reaction of pyrite with nitrate. The transfer of electrons during the transformation of nitrate to harmless dinitrogen (N<sub>2</sub>) gas proceeds through a series of four reduction steps (Pyenson, 2002, Gilboa-Garber, 1971).

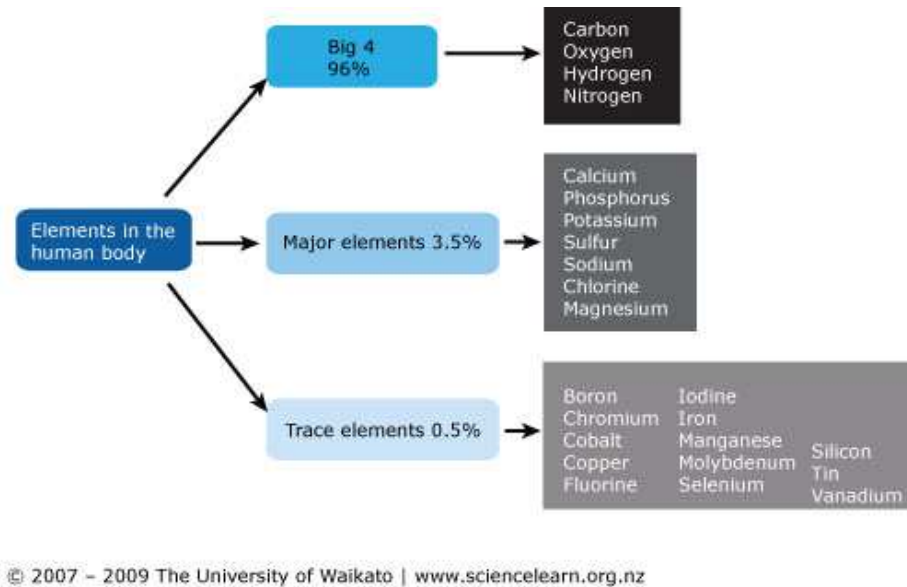


Nitrate can also reduced by organic compounds;



### 3.3 Mode of exposure and Biotoxic effect of trace elements

Roughly 96 percent of the mass of the human body is made up of just four elements: oxygen, carbon, hydrogen and nitrogen, with a lot of that in the form of water and the remaining 4 percent is the other periodic table of elements (Klaassen, 2007) (fig 2).

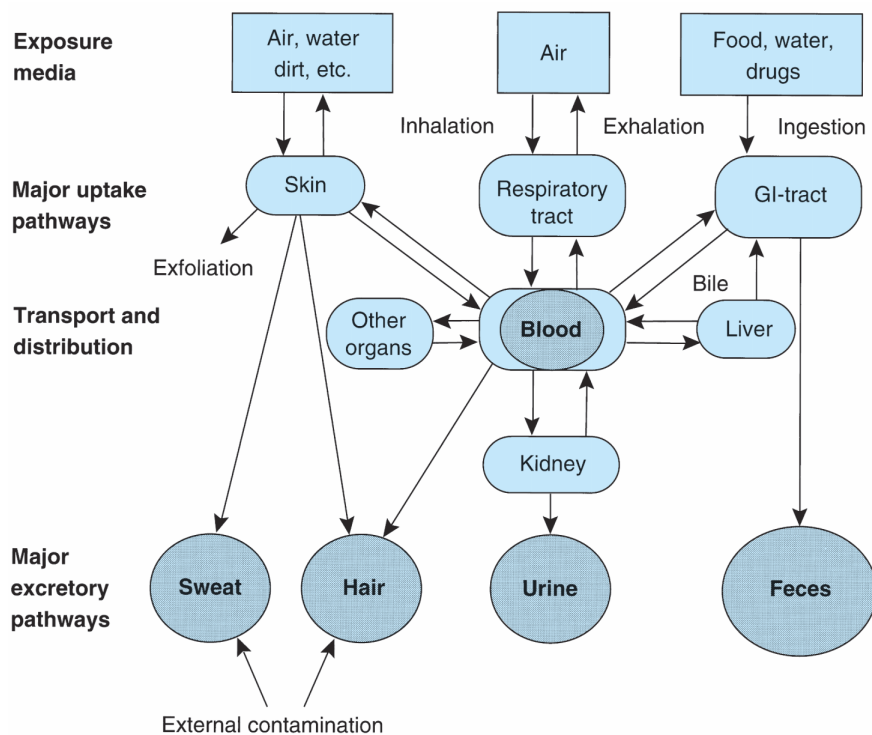


**Figure 2** Sketch showing distribution of chemical elements in human body system

Despite a very important role of trace elements in keeping the body working effectively, many of the them are required in only very small amounts. Trace elements have dose-effect relationships, that means both low intake and high intake of an element leads a biological functions decline. The toxicity of a given element depends on type of an element and its chemical structure in the diet(Selinus, 2005). Dose is the amount of metal within cells of organs manifesting a toxicological effect(Selinus, 2005). Not all elements can cause serious problem to health, it widely differs on the type of elements. Single measurements of dose may reflect recent exposure or longer-term or past exposure, depending on retention time in the particular tissue(Klaassen, 2007). There is a dose which no adverse effect will occur(WHO, 2011). A tolerable daily intake (TDI) is used to be derived for chemicals that give rise to such toxic effects. The TDI is an estimate of the amount of a substance in food, contact and drinking-water, expressed on a body weight basis (mg/kg of body weight), that can be ingested over a lifetime without appreciable health risk. Due to their interaction with body biochemistry,

when ingested in the acid medium of the stomach, they are converted to their stable oxidation states ( $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $As^{2+}$ ,  $As^{3+}$ ,  $Hg^{2+}$  and  $Ag^+$ ) and The combine with the body's biomolecules such as proteins and enzymes to form strong and stable chemical bonds(Duruibe et al., 2007).

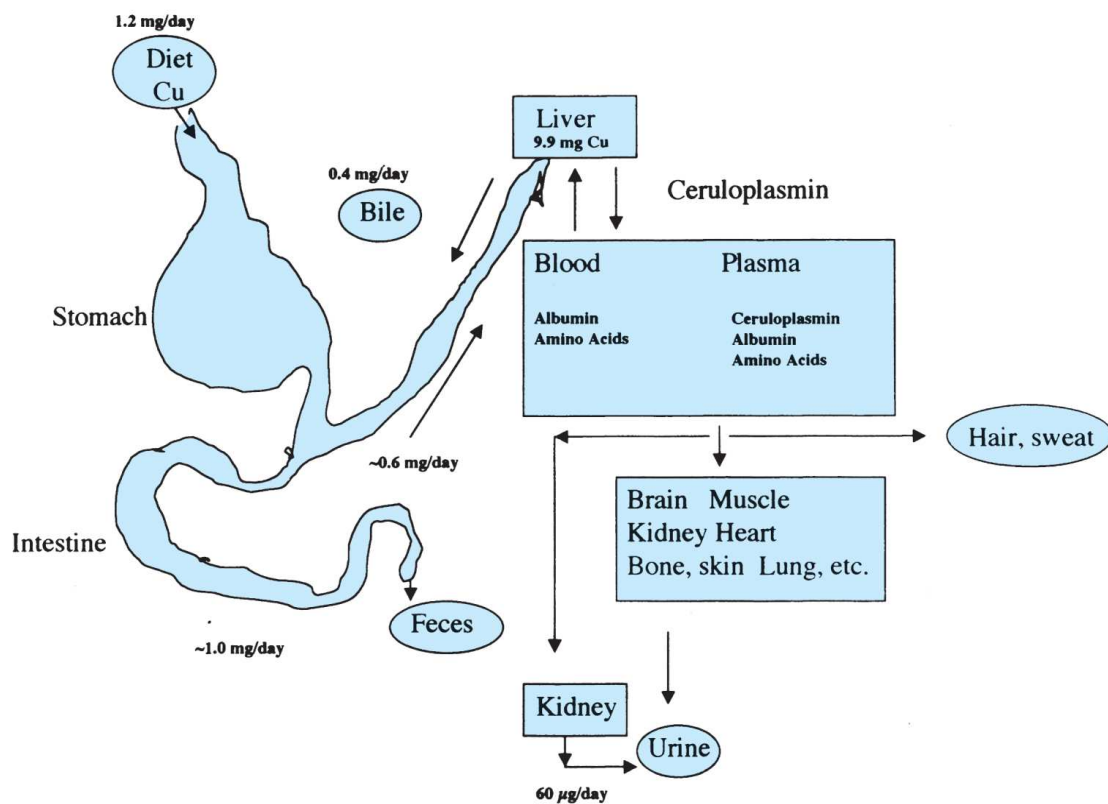
Different exposure route lead the availability of trace elements to human body system. The main exposure root for human body system are through contact with skin from air, water, dust etc., inhalation via air and ingestion via food, water and drugs (fig 3).



**Figure 3** Metabolism after exposure to chemical elements via skin absorption, inhalation and ingestion. The arrow indicates how metals are transported in human body system Elinder et al. 1994 cited by (Klaassen 2007)

The above figure (fig 2) shows both liver and kidney are the most exposed organs in trace element contamination during transport and distribution of human blood system(Klaassen, 2007). The liver is acting as detoxify for chemical elements to regulate the blood concentrations of trace elements (Ritland and Aaseth, 1986). That is why most of nonalcoholic liver diseases derives from the central role of the liver in trace element regulation(Loguercio et al., 2001). For example the liver receives copper from the intestine via the portal circulation and

redistributes the copper to the tissue via ceruloplasmin, albumin, and amino acids(Klaassen, 2007) ( fig 4).



**Figure 4** Overview of copper absorption, transport, and excretion (Klaassen 2007)

Most chemicals arising in drinking-water are of health concern only after extended exposure of years, rather than months(WHO, 2011). The basis on which drinking water safety is judged is by national standards or international guidelines(Duruibe et al., 2007). The most important of these are the WHO Guidelines for Drinking-Water Quality. Different studies suggested different type of trace elements that could cause liver disease based on guideline values. Elements documented related to liver diseases are; As, Pb, Se, Tm, Br, Ni, Cr, Cu, Al, F, Cd, Mg, Ag, Au Mn, Mo, Co, Tl, Zn, and Hg(Selinus, 2005, Klaassen, 2007, WHO, 2011, Udeh, 2004, Water, 1994, Fowler et al., 2011).



### **3.4 Problems in studying biotoxic effect of trace elements**

A complication in biotoxic effect study of trace elements appear because of most chemicals arising in drinking-water become a health concern only after extended exposure of years, rather than months (Klaassen, 2007).

Lack of specificity in identifying a responsible geochemical element for such toxicological effects is extremely difficult and sometimes impossible; it may be caused by a number of agents or even combinations of substances and also most metals affect multiple organ systems depending on the dose(Klaassen, 2007), (Craun and Calderon, 2005)

Different species of a given element have different health effects(Klaassen, 2007, Carroll. et al., 2002), for example Hexavalent chromium is highly toxic, whereas the trivalent form functions as an essential trace elements. Certain metals can form organometallic compounds involving covalent metal-carbon bonds and the patterns of disposition and toxicity of organic forms tend to differ from those of inorganic form(Selinus, 2005, Duruibe et al., 2007)

Toxicity of a metal vary from one organism to another based on many different factors including ; the characteristics of an individual organism, the route of exposure to the element, the type and form of the metal and the physical and chemical characteristics of the water where the exposure takes place(Klaassen, 2007). This is a challenge for using guideline values developed experiments on another species.

The guideline values are calculated separately for individual substances, without specific consideration of the potential for interaction of each substance with other compounds present. The interaction between different substances may result to detoxifying effect additive or synergistic effect (WHO, 2011, Selinus, 2005, Duruibe et al., 2007).

It is difficult to make a straightforward comparison of the results of geochemical analysis measurements(Brune et al., 1980) because geochemical element are compositional data (almost all data in geochemistry) which is a closed data system. But the chemical reactions are constrained by unmeasured or unconsidered geochemical elements (chemicals that are not consider in the analysis or simulation). Which mean geochemical data analysis needs a special treatment to open it and to consider other constraints (Aitchison, 1999b, Carranza, 2011).

### 3.5 Compositional data analysis

Compositions are positive vectors at which its component represents are a relative contribution of different parts of a whole; therefore their sum is a constant, usually 1 or 100. In geological science compositions are familiar and important because it appears in many geological datasets like chemical analysis, geochemical compositions of rocks, sand-silt-clay sediments etc. In 1897 Karl Pearson wrote a famous paper on spurious correlations and he was the first to point out dangers that may befall the analyst who attempts to interpret correlations between ratios whose numerators and denominators contain common parts. (Filzmoser, 2009) More recently, Aitchison, Pawlowsky-Glahn, S. Thió, and other statisticians have developed the concept of Compositional Data Analysis, pointing out the dangers of misinterpretation of closed data when treated with “normal” statistical methods. It is important for geochemists and geologists in general to be aware that the usual multivariate statistical techniques are not applicable to constrained data (Ricardo, 2008)

Developments in the statistical analysis of compositional data over the last two decades have made possible a much deeper exploration of the nature of variability, and the possible processes associated with compositional data sets from many disciplines (Thomas and Aitchison J., 2005). Compositional data (almost all data in geochemistry) are closed data meaning that they usually sum up to a constant (e.g weight percent, wt. %, ppm, ppb etc) and carry only relative information. The covariance structure of compositional data is strongly biased and results of many multivariate techniques become doubtful if they are not “open” (Filzmoser, 2009, Aitchison, 1999a).

Compositional data need a special treatment prior to correlation analysis (Filzmoser, 2009). The treatment is transformation of the data because computing especially correlations by using raw or log-transformed data is neither meaningful for compositional data (Ricardo, 2008, Lark, 2008). There are three log ratio compositional data transformation methods. Log ratios recognized the relative magnitudes and variations of components, rather than their absolute value, that provides a key to analysing compositional data. Aitchison (1982) introduced the additive-log ratio (alr) and centered-log-ratio (clr) transformations and later Egozencne (2003) the isometric-log-ratio (ilr) transformation. These transformation methods (alr, clr and ilr) is

used for a composition to represent as a real vector(Lark, 2008). One very important effect of “opening” a compositional dataset by using any of these transformations is that we get rid off all spurious correlations. This transformed data do contain unexpected correlations, but they are real(Ricardo, 2008).

Compositional data can be represented by constant sum real vectors with positive components, and these vectors span a simplex (eq1), defined as

$$\mathcal{S}^D = \left\{ \mathbf{x} = [x_1, x_2, \dots, x_D] \in \mathbb{R}^D \mid x_i > 0, i = 1, 2, \dots, D; \sum_{i=1}^D x_i = \kappa \right\}. \quad \text{eq1}$$

Where  $\mathcal{S}^D$  is considered to be the sample space of compositional data. The positive constant  $\kappa$  is arbitrary. Frequent values for  $\kappa$  are 1 (per unit), 100 (percent, %), 1000,  $10^6$  (ppm),  $10^9$  (ppb) etc

In alr D-1 of the component are divided by the remaining component and logarithms taken (eq2). The resulting log- ratios are real variables that can be analysed using standard statistical techniques

$$alr(x) = \left[ \log\left(\frac{x_1}{x_D}\right), \log\left(\frac{x_2}{x_D}\right), \log\left(\frac{x_3}{x_D}\right), \dots, \log\left(\frac{x_{D-1}}{x_D}\right) \right] \quad \text{eq2}$$

The clr coefficients are obtained by dividing the components by the geometric mean of the components and taking logarithms (eq3)

$$clr(x) = \left[ \log\left(\frac{x_1}{g(x)}\right), \log\left(\frac{x_2}{g(x)}\right), \log\left(\frac{x_3}{g(x)}\right), \dots, \log\left(\frac{x_D}{g(x)}\right) \right] \quad \text{eq3}$$

Where  $g(x)$  is the geometric mean

The expressions for the calculation of ilr (eq4) coordinates are more complex.

$$ilr(x) = (z_1, \dots, z_{D-1})^T, z_i = \sqrt{\frac{i}{i+1}} \ln \frac{i \sqrt{\prod_{j=1}^i x_j}}{x_i + 1} \quad \text{eq4}$$

Where  $i=1, \dots, D-1$ .

Correlation factors coefficients values are affected by data form and presence of censored values, outliers and multiple populations (Carranza, 2008a). For the data having skewed variables, logarithmic transformation normalizes the spurious correlation caused by outliers. Correlation of log transformed data is better than the raw data. Even though the log transfor-

mation improves the problem caused by skewed variables, the derived correlation coefficients could severely mislead because the variables are compositional variables.

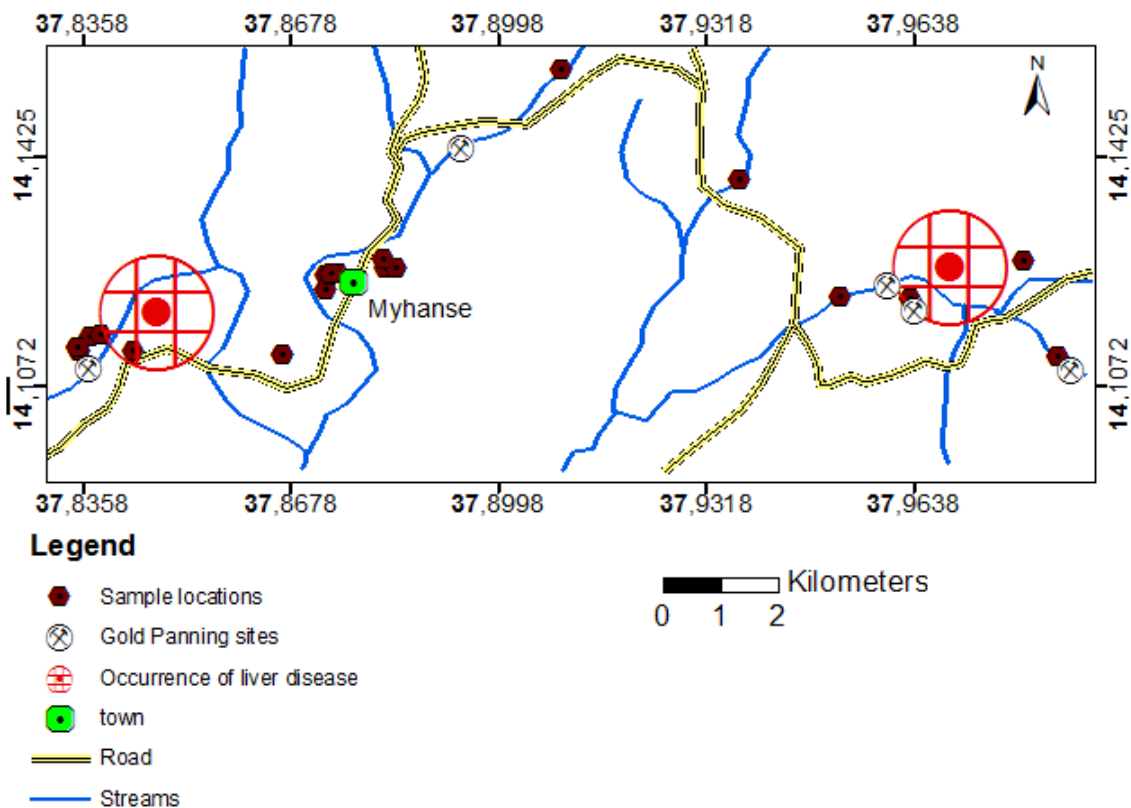
In summary, trace element toxicology is an emerging and complex discipline. For a better understanding of the source, mobilization, hydrochemical environments and health effects of trace elements needs special way of approach. A better understanding of the association between trace element in the source rock and dissolved water solution is crucial for a better understanding of detoxifying and additive and synergetic effects of trace element contamination. A better understanding of natural chemical environment and effects of anthropogenic activities on redoxcline condition of ground water is needed while this kind of process might increases the dissolution rate of trace elements that increases health risks. As chemical elements are compositions it needs a special attention in analysis of geochemical elements, special data analysis method like compositional data analysis in contamination study is recommended.

## 4. METHODOLOGY

The methodology used for this thesis work; field data collection, laboratory analysis and statistical data analyses are described as follows.

### 4.1 Field data Collection

Field data collection was conducted during July 2013. During this field work 16 water 16 soil and 14 rock samples were collected. The sampling sites were selected based on the distribution of potential pollutant sources to the liver disease incidence area (by interviewing the local people about the incidence of the liver disease and their source of drinking water) and the availability and accessibility of water source for the community. At each water sampling location, soil and rock sample were taken. In conjunction with sampling, close field observation were made on the types of geology, anthropogenic activities like artesian gold mining sites, physical land degradation and supported by photographs.



**Figure 5** Location maps of field data sampling

The ground water samples were taken from shallow hand dug wells and streams. Each sample was filtered and collected in 100 ml polyethylene bottle, and the sampling bottle was rinsed repeatedly with distilled water before taking the samples. After sampling the bottles were tightly covered with caps and sealed with tap to minimize oxygen contamination and the escape of dissolved gases. At each sample station two water sample were taken; one bottle with acidified by a drop of nitric acid to decrease the activity of cations and another one without any acidification. The pH of the water samples were measured on site. The samples are kept in cold place to minimize chance of chemical reaction which can result in precipitation of dissolved elements.

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 samples were taken from stream that has flowing water at which the local people used for drinking water and gold panning. Most of stream sediment samples are taken from the same site where water sample is collected. The samples (about 300 gram each) were collected using a shovel tool and store in to a clean plastic bags.

Representative rock samples were collected from all lithological units associated with water sample locations. The lithology, structures, mineralation, quartz veins and alteration intensity of the rocks has been studied in the field. Besides to field observation, Collection and review of previous data on the geology area were performed. Topographic map at 1:50,000 scale was used to illustrate the drainage and physiographic of the area. Landsat satellite image were used to map the spatial distribution of different lithologies in addition to the pervious unpublished geological reports and filed observations. The major lineaments in the study area are mainly inferred from the satellite image and a hillshade generated from 30m vertical resolution digital elevation map.

## **4.2 laboratory sample analysis**

Preparation of samples (all water, soil and rock) for chemical analysis, analysis of major anions and cations and XRD mineralogy analysis of rock and soil samples were done at university of Oslo, department of geosciences but chemical analysis of trace elements was done at Activation Laboratories Ltd (Actlabs), Canada.

#### **4.2.1 Water sample laboratory analysis**

Major anions and cations were measured using Ion Chromatography, it were measured from different duplicate samples of each sample station; cations from acidified sample and anions from non-acidified water sample. pH of each water sample were also measured in the lab.

For trace element analysis acidified water sample were used. The analysis of these trace elements on water sample was done by Inductively Couple Plasma Mass Spectrometer (ICP-MS) at Activation Laboratories Ltd (Actlabs), Canada. Before analysis water sample were filtered and acidified up to 2% by nitric acid. Because of the instrument is working with low total dissolved solid content (<0.05%), our sample which have TDS value up to 0.14 % were diluted three times.

#### **4.2.2 Rock and soil laboratory data analysis**

Rock samples were first crushed in stain less steel jaw crusher and then powdered in an agate meal and pulverizing to be a homogenous powder prior to for chemical analysis. Trace elements analysis was carried out after an extraction using aqua regia digestion solution. This leach uses a combination of concentrated hydrochloric and nitric acids to leach sulphides, some oxides and some silicates. After aqua regia digestion, analyses were done by Inductively Coupled Plasma - Optical Emission Spectrometry (ICP/OES) instruments.

To identify the organic compounds in two of the graphite shiest sample rocks were analyzed using organic solvent (in this case a mix if dichloromethane and methanol at 93:7 v/v ratio). The extracts are then fractionated by Iatrosan Thin Layer Chromatography-Flame Ionization Detector (TLC-FID) into Saturated (SAT), Aromatic (ARO) and Polars (POL).

### **4.3 Statistical data analysis**

Analytical treatment of data was made mainly in Excel. Statistical analysis such as mean, standard deviation skewedness was done for exploratory analysis of the data. Data obtained from water samples were compared with WHO standards to see whether or not they were within the recommended range thus safe to human.

The possible relationships between trace elements were computed by conducting correlation analysis. Quantitative measures of linear association between the different parameters were

obtained from the correlation coefficients of pairs of parameters. In the correlation analysis we used both; “normal” statistical analysis (using row data) and compositional data analysis (on transformed data).

Pearson's correlation coefficient is defined between two variables, defined as the covariance of the two variables divided by the product of their standard deviations:

$$\rho_{X,Y} = \frac{\text{cov}(X, Y)}{\sigma_X \sigma_Y} = \frac{E[(X - \mu_X)(Y - \mu_Y)]}{\sigma_X \sigma_Y},$$

And it works in unconstrained data system (the variables can varies from  $+\infty$  to  $-\infty$ ) but geochemical variables are a compositional data that are constrained (the variables or components can varies within closed system i.e. the sum of all variables should be constant), the components are some part of the whole and recorded in closed form (ppm).

From the three logratio transformations methods (alr, clr and ilr) which have been introduced to transform compositional data to an unconstrained real space (Filzmoser and Hron, 2009, Aitchison, 1999a), we used the additive logratio and centred logratio transforming method (fig 17). Isometric log ratio (ilr) coordinates are more complex and difficult to interpret geologically and has the disadvantage that the resulting new variables are no longer directly interpretable in terms of the originally entered variables.(Lark, 2008)

In compositional data analysis the sum of the variables for each sample should be constant (1, 100% etc). But our measurement is not the whole geochemical element analysis. It does not sum up to a constant. Inter geochemical correlation is not only constrained by measured geochemical elements it also influenced by unmeasured elements which are components of the sample. To take in account this problem (the composition sum should be constant and the influence of unmeasured elements in correlation analysis), we add one dimension to the seven geochemical element variables called the reminder (R).

$R = 1,000,000 - (\text{As}(\text{ppm}) + \text{Cu}(\text{ppm}) + \text{Fe}(\text{ppm}) + \text{Mn}(\text{ppm}) + \text{Pb}(\text{ppm}) + \text{Sb}(\text{ppm}) + \text{Zn}(\text{ppm}) + \dots)$ . (i.e the measurement is parts per million (ppm) and R remains in parts of per million(ppm)).



$$alr(x) = \left[ \log\left(\frac{As}{R}\right), \log\left(\frac{Fe}{R}\right), \log\left(\frac{Mn}{R}\right), \log\left(\frac{Pb}{R}\right), \log\left(\frac{Sb}{R}\right), \log\left(\frac{Cu}{R}\right), \log\left(\frac{Zn}{R}\right), \dots \right] \dots \dots \text{eq5}$$

For additive logratio transformation

$$clr(x) = \left[ \begin{array}{l} \log\left(\frac{As}{g(x)}\right), \log\left(\frac{Fe}{g(x)}\right), \log\left(\frac{Mn}{g(x)}\right), \log\left(\frac{Pb}{g(x)}\right), \log\left(\frac{Sb}{g(x)}\right), \log\left(\frac{Cu}{g(x)}\right), \\ \log\left(\frac{Zn}{g(x)}\right), \dots, \log\left(\frac{R}{g(x)}\right) \end{array} \right] \dots \dots \text{eq6}$$

Where g(x) is the geometric mean for centered log transformation

CoDaPack software was used to transform the data set. It is a visual basic freeware Excel for windows-based package (Henestrosa, 2008). It offers three types of transformation, the Centered Log-Ratio transformation (clr), the Additive Log-Ratio transformation (alr), and the Isometric Log-Ratio transformation (ilr).

The multivariate data analysis was done by PAST statistical analysis software. Principal components with significant eigenvalues and cluster of the first two components were used. To identify the relation between lithology and geochemical elements boxplots were done by R statistics.

#### 4.4 Spatial association of trace elements with lithology

In order to understand the relationship between different trace elements in ground water and the type of lithology of the area, we used box plots with lithology. Box plots are important and strong graphical statistical to explore the possible relationship between variables. The box plots were between concentrations of elements at which its concentration is above maximum tolerable limit with lithologies that are mapped at which the sample were taken in the area. Also quantile maps with lithology are used to see the spatial distribution and association with lithology of such elements.

#### 4.5 Simulation of redox reaction of nitrate and carbon on dissolution of trace elements in the ground water

The simulation is a batch reaction as incremental-reactions. The batch reaction performs in

20 steps of incremental reaction step with the first step add a given mole of added reactants and the intermediate results are saved as the starting point for the next step. The total amount of each reactant added at any step in the reaction is the reaction amount times the relative stoichiometric coefficient of the reactant. The simulation performs in three different cases of batch reaction; the first one is a redox reaction of sulfide with nitrate, the second case is a reaction with redox reaction with organic carbon and the third case is a reaction with both nitrate and organic carbon. The simulation also considers the excess of iron would perform precipitation as FeS.

## **5. GEOLOGY**

### **5.1 Regional geology**

Regionally, the area is part of the pan – African (Neo – Proterozoic) Arabian - Nubian shield, where dominantly green schist facies acidic to basic Metavolcanics, linear belts of mafic and ultra-mafic masses of serpentinite, talcose rock, pyroxenite and gabbro and associated pre to syn tectonic calc- alkaline granitoid bodies and post tectonic granites are exposed. Bodies of folded supra crustal meta-sedimentary marine and fluvial assemblages form other distinct entities in the shield (Shackleton, 1994).

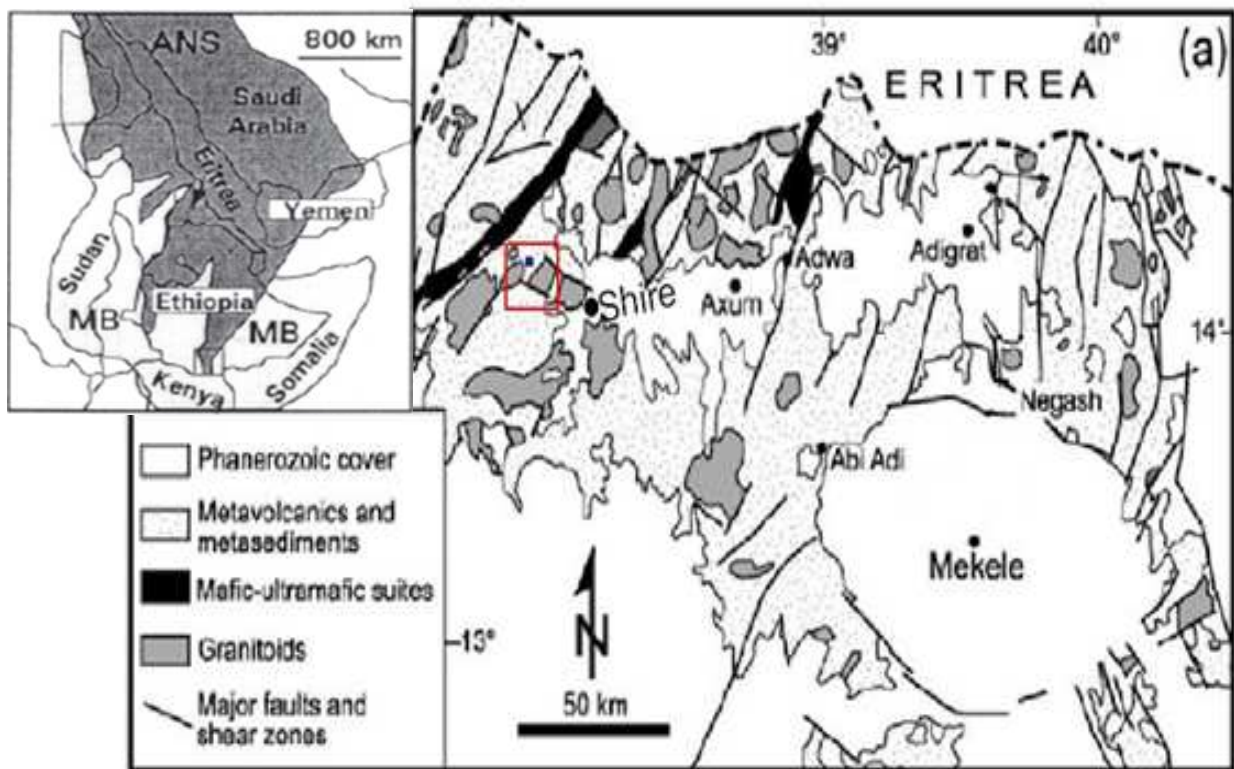
The Arabian Nubian Shield which extends from Saudi Arabia and Egypt in the North and down to Ethiopia is believed to have developed by Phanerozoic type plate – tectonic process during the 950-500 Ma, Pan – Africa Orogeny (Vail, 1985). The process involved repeated closure and accretion of Intra – Oceanic island arc basins along suture zones decorated by linear belts of remnants of suture dismembered ophiolitic complex, (Vail, 1985, Gass, 1981).

A sharp tectonic contact break produced by a series NNE-SSW faults demarcating the ultra-mafic body and metavolcano-sedimentary units. Across this topographic Break, sharp stereographic, structural and metamorphic discontinuities occur (Tadesse et al., 1999) .

The major structural features associated with mafic and ultramafic rocks are characterized by fold and thrust type tectonics whose asymmetry indicates its association with oblique compression (Tadesse et al., 1999). These features are very similar to the structural features described in collision / accretion related setting in the Arabian - Nubian Shield of Egypt

(Abdelsalam and Stern, 1993, Gass, 1981, BERHE, 1990). Generally kinematic indicators showed that the mafic – ultramafic rocks are abducted due to thrusting with a NW verge and it could represent a possible intra- oceanic suture zone (Asrat et al., 2004).

The other structural feature is a NE – SW ductile and brittle ductile shear zone; the shear zone modified and transposed the preceding structural elements and present structural set up of the area is represented by this deformational event (Asrat et al., 2004, Tadesse et al., 1999). The nuclei of this shear zone are marked by sericite, chlorite, oxidized sulfides and seldomly quartz srengrers and chert. Asymmetrically deformed pyrite crystal and quartz vein indicate a horizontal strike slip with dextral vertocity.

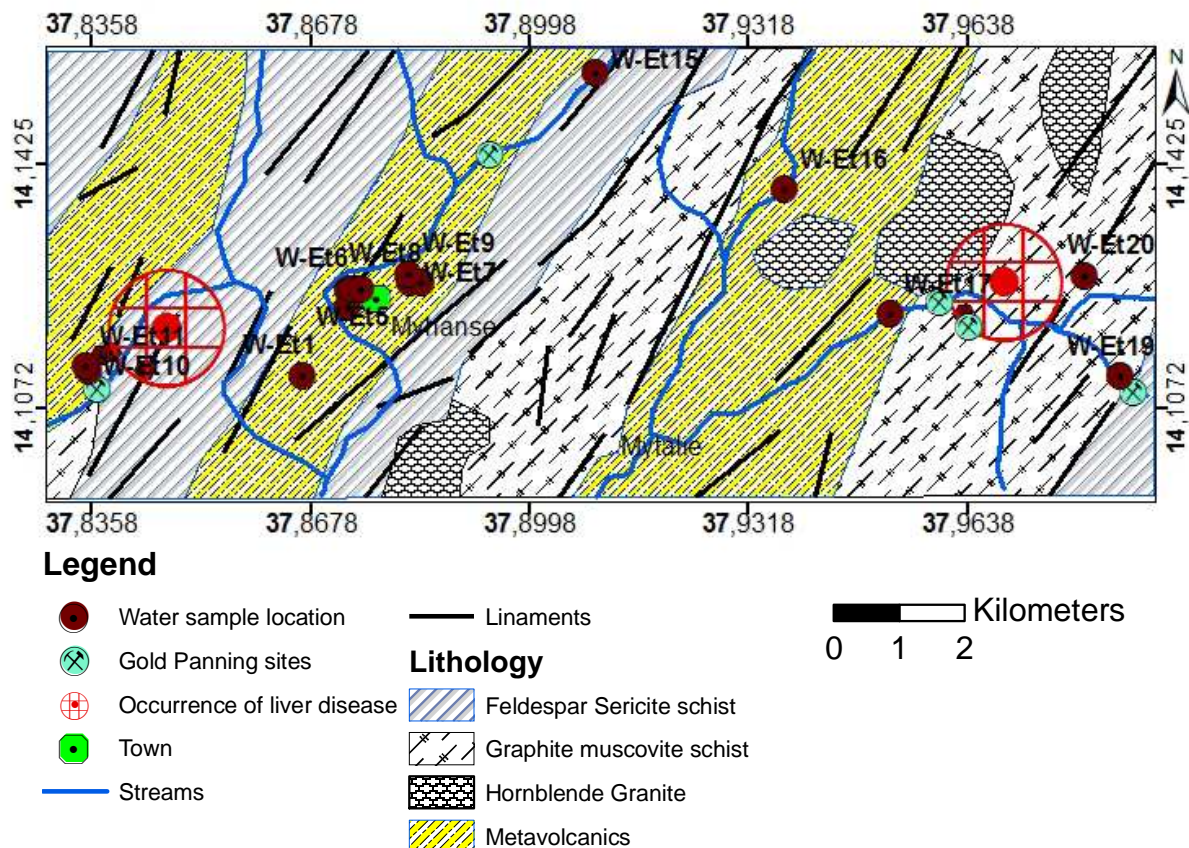


**Figure 6** Location of the study area on the geological maps of northern Ethiopia. Inset shows the inter fingering relationship of the Arabian – Nubian Shield (ANS) and the Mozambique Belt (MB) and location of Precambrian rocks of northern Ethiopia(modified from(Asrat et al., 2004)).

## 5.2 Geology of the study area

### 5.2.1 Lithology

The main lithological units in the study area are mainly covered by metamorphic rocks which include: feldspar sericite schist, graphite- muscovite schist, metavolcanics (includes basic to acidic volcanic rocks, metagreywackes, metabreccia and fine-grained, tuffaceous clastics) and circular shape hornblende granite (fig 7). Aplitic dykes and quartz vein and veinlets are also exposed in different parts of the area. Different lithologies are allied parallelly in north east to south west direction and intruded by granites, aplitic dykes and quartz veins.



**Figure 7** Geological map of study area (Myhanse).

Metavolcanics: the metavolcanic unit is found in contact between the quartz - graphite schist unit in its eastern part, and between muscovite schist in the northwestern and central part of the study area. It is moderately weathered, highly foliated, greenish grey and pinkish in color



and fine grained in texture. In places, rounded to angular clasts (~ 3cm) of intermediate to felsic compositions are found with in this rock unit. In some part of the study area this lithological units show chlorite talc schist, which is silvery gray to greenish color, fine grained in texture and have shiny surfaces.

**Feldspar Sericite Schist:** It is exposed mainly in the north western of the study area in contact with metavolcanic units. This unit is slightly oxidized, sericitized, chloritized and locally silicified and it is gray with pale greenish yellow in color and fine grained in texture. Phyllite and graphite schist are encountered as intercalation in this unit.

**Graphite –Muscovite Schist:** it is dark gray, fine grained, and strongly foliated, less feasible with lustrous yellow sheen (fig 8). It is found in the central, eastern and southwestern end of the study area, which is in contact with metavolcanic and feldspar sericite schist (fig 7).



**Figure 8** gray and foliated Graphite -Muscovite Schist

Hornblende Granite: it appear as subcircular to elliptical shape exposed at northeastern and southern part of the study area; characterized by coarse grained, pale to pink colored locally porphyritic at the core and medium grained at the marginal zone.

Granitic Dikes: it is light pink color, course to medium grained, which is composed of quartz, feldspar and other dark grey color minerals. It is out cropped concordant to discordant to the foliation of the metamorphic units of the area. It reaches from 2m up to 30m width and about 150 m and above in strike length.

### **5.2.2 Geologic structures**

The lithology of the study area is affected by different structures such as folds, faults, fractures and shear zones. The major structural feature in the area is that northeast – southwest striking lineaments and composite foliations (fig 7).

*Foliations* are the major prominent structures observed. Feldspar sericite schist (including phyllite) units are highly foliated, whereas the metavolcanics are moderately foliated. This foliation commonly strikes parallel to the main geological lineaments which is northeast to southwest direction (fig 8 &7). Northeast trending lineations, quartz veinlets and stringers are also occurring in the study area (fig 10).

*Shear zone*: the presence of shear zone is identified in the north western part of the study area with in the metavolcanic unit. This shear zone is a brittle - ductile type and is generally narrow (150 to 200m wide) and extends for over few tens of km along strike. Horizontal plunging mineral aggregate minerals and elongation lineations in the shear zone invariably indicate a sinistral strike slip sense of displacement.

*Faults:* strike slip faults are observed mainly on the eastern part of the area affecting the intermediate metavolcanic and graphite schist units (fig 9). These faults are detected on the outcrop scale by the displacement of quartz veinlets, lithological shifting and also the development of creeks along the plane of displacement or line of weakness. The fault plane strike approximately N45° E and dip east wards. The lateral component of displacement is a dextral sense and in the order of 30 to 50m.



**Figure 9** View towards northwest on NE trending fault with dextral sense of displacement

*Joints* are also the common fractures features observed on lithological units and main dominantly in metavolcanic unites. The general orientation of this joints are parallel the major lineaments and width vary from tight up to 5m and they continued for hundreds of meters in a discontinuous manner. Some of the joints and fractures are filled by quartz veins and stringers (a thin discontinuous mineral vein).

*Quartz veins:* two main stage of quartz vein have been detected based on their intersection relationship and their occurrence with respect to the foliation of host rocks. These are ≈N35°E trending, moderately deformed, least abundance and thin (≈ 0.5 – 2 cm thick),

N70°E highly deformed quartz veins with up to 3cm thick (Figure 9). Alteration such as sericitization, chloritization and talcification are observed in the quartz and most of the quartz veins are fractured or brachiated.



**Figure 10** Quartz vein and Joints with in the metavolcanic unit

### **5.2.3 Mineralization and alterations**

Asgede Tsimbla sub catchment area is known for the occurrence of gold. Filed observation and unpublished geological reports shows the presence of graphite, sericite, chlorite, talc and biotite minerals.

Gold mineralization: there is occurrence of both primary and placer gold deposits. In many areas where there is shearing, extensive panning for gold by the local people has been practiced. They find a number of fine grained angular gold grains. Investigations in these sheared zones shows that the gold mineralization is associated with thin and deformed quartz veins and stringers in the shear zone and it is suggested that the mineralization is associated with



one the shearing episodes in the area(Tadesse et al., 1999).There is also an extensive artisanal gold mining along the course rivers and adjacent terraces by the local people are shown in the figure below (Figure 10).



**Figure 11** Artesinal gold mining practices in Asgeda Tsimbla sub catchment area

**Table 1** XRD analysis result of rock and soil samples

Sample code	Minerals	Formula	Percentage
R-Et-1	Labradorite	Ca <sub>0.004</sub> Fe <sub>0.912</sub> Mg <sub>1.07</sub> Mn <sub>0.012</sub> O <sub>4</sub> Si	29.94 %
	Diopside-subsilicic	Ca Fe <sub>0.597</sub> Mg <sub>0.733</sub> O <sub>6</sub> Si <sub>1.67</sub>	34.84 %
	Anorthite	Al <sub>1.911</sub> Ca <sub>0.716</sub> Mn <sub>0.196</sub> Na <sub>0.045</sub> O <sub>8</sub> Si <sub>2.089</sub>	35.22 %
R-Et-2	Quartz	O <sub>2</sub> Si	98.65 %
	Pyroxene-ideal	Mg O <sub>3</sub> Si	1.35 %
R-Et-3	Sodalite	Al <sub>6</sub> Cl <sub>2</sub> Na <sub>8</sub> O <sub>24</sub> Si <sub>6</sub>	59.73 %
	Chromite	Cr <sub>2</sub> Fe O <sub>4</sub>	14.51 %
	Unknown	Cl <sub>6</sub> Cs <sub>2</sub> Se	12.94 %
	Unknown	O <sub>4</sub> V <sub>2</sub> Zn	12.83 %
R-Et-4	Lizardite	H <sub>4</sub> Mg <sub>3</sub> O <sub>9</sub> Si <sub>2</sub>	75.10 %
	Unknown	Cr F <sub>3</sub>	22.53 %
	Unknown	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> Zn	1.76 %
	Unknown	C <sub>5</sub> H <sub>8</sub> Au Cl N <sub>2</sub>	0.61 %
R-Et-5	Quartz	O <sub>2</sub> Si	52.11 %
	Oligoclase	Al <sub>1.179</sub> Ca <sub>0.179</sub> Na <sub>0.821</sub> O <sub>8</sub> Si <sub>2.821</sub>	32.52 %
	Unknown	C <sub>60</sub> H <sub>120</sub> N <sub>4</sub> O <sub>10</sub> S <sub>8</sub> Sn <sub>4</sub>	11.05 %
	Unknown	C <sub>6</sub> H <sub>114</sub> B <sub>28</sub> Mn <sub>4</sub> O <sub>132</sub> V <sub>10</sub>	4.31 %
R-Et-8	Quartz	O <sub>2</sub> Si	41.37 %
	Albite	Al Na O <sub>8</sub> Si <sub>3</sub>	34.10 %
	Muscovite	Al <sub>2.568</sub> F <sub>0.28</sub> Fe <sub>0.13</sub> H <sub>1.72</sub> K <sub>0.84</sub> Li <sub>0.13</sub> Mg <sub>0.01</sub> Na <sub>0.14</sub> O <sub>11.72</sub> Rb <sub>0.02</sub> Si <sub>3.192</sub>	22.41 %
	Unknown	C <sub>10</sub> H <sub>8</sub> Cu <sub>2</sub> N <sub>13</sub>	2.12 %
R-Et-9	Albite	Al <sub>1.02</sub> Ca <sub>0.02</sub> Na <sub>0.98</sub> O <sub>8</sub> Si <sub>2.98</sub>	43.66 %
	Quartz	O <sub>2</sub> Si	20.87 %
	Emilite	Bi <sub>11</sub> Cu <sub>5.99</sub> Pb <sub>5</sub> S <sub>24</sub>	19.15 %
	Muscovite	Al <sub>2.16</sub> F <sub>0.58</sub> Fe <sub>0.42</sub> H <sub>1.42</sub> K <sub>0.97</sub> Li <sub>0.38</sub> Mg <sub>0.01</sub> Na <sub>0.02</sub> O <sub>11.42</sub> Rb <sub>0.01</sub> Si <sub>3.28</sub>	15.29 %
Unknown	Mg Mn O <sub>4</sub> Si	1.03 %	
R-Et-10	Albite	Al <sub>1.02</sub> Ca <sub>0.02</sub> Na <sub>0.98</sub> O <sub>8</sub> Si <sub>2.98</sub>	57.45 %
	Quartz	O <sub>2</sub> Si	39.08 %
	Unknown	Cl <sub>4</sub> K <sub>3</sub> N O <sub>3</sub> Zn	3.48 %
R-Et-11	Quartz	O <sub>2</sub> Si	67.70 %
	Muscovite	Al <sub>2.64</sub> Fe <sub>0.06</sub> H <sub>0.3</sub> K <sub>0.92</sub> Mg <sub>0.06</sub> Na <sub>0.08</sub> O <sub>12</sub> Si <sub>3.2</sub> Ti <sub>0.06</sub>	26.69 %
	Unknown	C <sub>12</sub> H <sub>38</sub> Cl <sub>2</sub> N <sub>4</sub> Ni O <sub>4</sub>	3.45 %
	Goethite	Fe H O <sub>2</sub>	2.16 %
R-Et-11-2	Quartz	O <sub>2</sub> Si	45.30 %
	Graphite	C	51.45 %
	Djurleite	Cu <sub>31</sub> S <sub>16</sub>	3.25 %
R-Et-13	Quartz	O <sub>2</sub> Si	32.32 %
	Albite	Al <sub>1.02</sub> Ca <sub>0.02</sub> Na <sub>0.98</sub> O <sub>8</sub> Si <sub>2.98</sub>	27.23 %
	Muscovite	Al <sub>2.4</sub> Fe <sub>0.22</sub> H <sub>2</sub> K <sub>0.9</sub> Mg <sub>0.16</sub> Na <sub>0.07</sub> O <sub>12</sub> Si <sub>3.2</sub> Ti <sub>0.02</sub>	25.56 %
	Unknown	C <sub>20</sub> H <sub>42</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>7</sub> S	14.89 %
R-Et-18	Quartz	O <sub>2</sub> Si	46.70 %
	Albite	Al Na O <sub>8</sub> Si <sub>3</sub>	23.77 %

	Epidote unknown	Al <sub>2.16</sub> Ca <sub>2</sub> Fe <sub>0.84</sub> H O <sub>13</sub> Si <sub>3</sub> Ca <sub>2</sub> O <sub>12</sub> Rb <sub>2</sub> S <sub>3</sub>	16.65 % 12.89 %
R-Et-19	Quartz Graphite Unknown (NH <sub>4</sub> )SH Murdochite	O <sub>2</sub> Si C Fe <sub>1.176</sub> O <sub>5</sub> P N S Cu <sub>6</sub> O <sub>8</sub> Pb	35.25 % 25.72 % 19.47 % 18.31 % 1.24 %
R-Et-20	Quartz Graphite Unknown Otavite InAs	O <sub>2</sub> Si C O <sub>7</sub> P <sub>2</sub> Si C Cd <sub>0.55</sub> Mg <sub>0.45</sub> O <sub>3</sub> As In	41.69 % 31.77 % 24.88 % 1.27 % 0.39 %
S-Et-1	Albite Unknown Vermiculite Unknown	Al Na O <sub>8</sub> Si <sub>3</sub> C <sub>16</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>8</sub> O <sub>8</sub> Zn H <sub>2</sub> Mg <sub>3</sub> O <sub>12</sub> Si <sub>4</sub> C <sub>6</sub> H <sub>5</sub> O <sub>3</sub> P Pb	77.19 % 19.09 % 3.02 % 0.70 %
S-Et-8	Quartz Albite Unknown	O <sub>2</sub> Si Al Na O <sub>8</sub> Si <sub>3</sub> C <sub>27</sub> H <sub>31</sub> Cl Cu N <sub>3</sub> Na O <sub>6</sub>	79.55 % 16.90 % 3.56 %
S-Et-10	Quartz Unknown Proustite Unknown Vermiculite	O <sub>2</sub> Si C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> Ag <sub>3</sub> As S <sub>3</sub> C <sub>14</sub> H <sub>10</sub> Cu N <sub>2</sub> O <sub>8</sub> H <sub>2</sub> Mg <sub>3</sub> O <sub>12</sub> Si <sub>4</sub>	53.83 % 40.14 % 4.75 % 0.79 % 0.48 %
S-Et-11	Quartz Albite Unknown Unknown	O <sub>2</sub> Si Al <sub>1.02</sub> Ca <sub>0.02</sub> Na <sub>0.98</sub> O <sub>8</sub> Si <sub>2.98</sub> C <sub>27</sub> H <sub>31</sub> Cl Cu N <sub>3</sub> Na O <sub>6</sub> C <sub>6</sub> H <sub>7</sub> N <sub>7</sub> O <sub>3</sub>	56.79 % 20.30 % 14.62 % 8.29 %
S-Et-13	Quartz Albite Epidote Unknown Srebrodolskite	O <sub>2</sub> Si Al <sub>1.02</sub> Ca <sub>0.02</sub> Na <sub>0.98</sub> O <sub>8</sub> Si <sub>2.98</sub> Al <sub>2.17</sub> Ca <sub>2</sub> Fe <sub>0.81</sub> H O <sub>13</sub> Si <sub>3</sub> C <sub>14</sub> H <sub>22</sub> N <sub>12</sub> O <sub>6</sub> Al <sub>0.135</sub> Ca <sub>2</sub> Fe <sub>1.865</sub> O <sub>5</sub>	33.17 % 33.15 % 28.65 % 3.66 % 1.37 %
S-Et-18	Quartz Albite Unknown Fourmarierite	O <sub>2</sub> Si Al Na O <sub>8</sub> Si <sub>3</sub> C <sub>70</sub> H <sub>144</sub> Ba <sub>6</sub> N <sub>6</sub> O <sub>6</sub> S <sub>11</sub> H <sub>10</sub> O <sub>19</sub> Pb U <sub>4</sub>	65.44 % 30.85 % 2.31 % 1.39 %
S-Et-20	Quartz Cuprite Graphite Vermiculite	O <sub>2</sub> Si Cu <sub>2</sub> O C H <sub>2</sub> Mg <sub>3</sub> O <sub>12</sub> Si <sub>4</sub>	36.85 % 1.61 % 21.82 % 0.17 %

The type of alterations observed in the study are; sericitization, chloritaization, oxidization of sulphides and silicification in the sheared and schistosed rocks. Epidotization and chloritaization in the metavolcanics and graphitization on Graphite –Muscovite Schist are the major alteration minerals. This alteration minerals are also observed in the XRD laboratory study listed on above table (table 1). There are also unknown organic minerals, which are common minerals especially in the area where graphite schist is dominated (table 1). This organic minerals also shows sequester of trace elements in the form of metallo-organic compounds (Selinus, 2005). Besides to sulfide minerals oxide minerals like Cuprite are among the common minerals that contain trace elements. The soil samples also show alteration minerals like vermiculite.

**Table 2** Results of Iatroscan TLC-FID on graphite schist rocks (the extracts are then fractionated by Iatroscan Thin Layer Chromatography-Flame Ionization Detector (TLC-FID) into Saturated (SAT), Aromatic (ARO) and Polars (POL).)

Sample ID	Extract yield (mg/g rock)				Extract concentrations (%)		
	SAT	ARO	POL	TOTAL	SAT	ARO	POL
R-ET-19	1.28	0.000062	4.39	5.66	22.51	0.0011	77.48
R-ET-20	1.17	0	4.49	5,65	20.63	0	79.37

The Above table (table 2) shows analysis of organic compounds on two graphite schist rock samples. It is very clearly shown that these two samples have no any aromatic extract. Aromatic compounds are organic compounds with one or more benzene rings in their chemical structure. Because of their high solubility, low-molecular-weight aromatics such as benzene and toluene are readily washed from the rock by circulating groundwater. Even sample R-ET-20 can be said that it contains zero percentage of aromatics. Since the saturates are also very low (normally should be more than 40 to 50% of the total extract depending on the oil composition), these samples are surface samples that have been exposed to the surface during geological times for the saturates to be easily oxidized by the atmospheric oxygen and to be biodegraded by bacterial activity and for the aromatics to be easily washed by water. The high concentration of polar compounds could indicate that the samples contain high concentration of sulfur.

## 6. Result and discussion

### 6.1 Major ions and potable quality of water in the study area

The analytical results and summery statistics (mean, minimum, maximum and standard deviation) of major ions in water samples from Asgede Tsimbla sub catchment area are presented below in table3.

**Table 3** The analytical results and summery statistics of major ions in water samples (all in ppm) (where TDS= total dissolved substance and E:B= electron balance).

S.no	F	Cl	SO <sub>4</sub>	Br	NO <sub>3</sub>	HCO <sub>3</sub>	Na	K	Mg	Ca	pH	TDS	E.B
W-Et1	0,4	47,4	17,5	0,6	<b>42,1</b>	<b>646,8</b>	14,3	3,6	156,0	35,3	8,6	963,9	8,2
W-Et2	0,3	43,5	36,1	0,6	<b>92,9</b>	390,5	13,1	6,6	120,0	40,8	8,6	744,4	12,3
W-Et3	0,3	4,4	3,9	0,5	<b>29,6</b>	543,1	6,4	0,5	136,0	11,8	8,2	736,4	11,5
W-Et4	0,3	44,9	27,3	0,6	<b>85,2</b>	390,5	9,6	0,8	114,0	38,9	8,1	712,0	10,1
W-Et5	0,3	50,0	25,9	0,6	<b>64,3</b>	390,5	7,6	0,7	9,7	40,4	8,6	590,0	4,9
W-Et6	0,3	<b>143,0</b>	70,9	0,8	<b>351,0</b>	463,8	13,7	0,6	197,0	71,6	8,5	<b>1312,6</b>	4,1
W-Et7	0,6	14,5	176,0	0,0	<b>59,8</b>	299,0	141,0	0,9	38,5	35,0	8,5	765,9	5,5
W-Et8	0,5	11,6	263,0	0,0	<b>32,0</b>	262,4	109,0	0,5	43,2	75,6	7,8	797,8	6,5
W-Et9	1,0	27,6	185,0	0,6	<b>91,3</b>	256,3	89,0	0,9	50,9	61,3	8,0	763,8	4,0
W-Et10	0,7	52,6	17,9	0,0	0,6	<b>677,3</b>	139,0	0,7	34,4	83,0	7,5	1006,2	0,4
W-Et11	0,8	93,6	23,0	0,5	0,0	<b>671,2</b>	139,0	1,1	32,3	99,4	7,5	1060,9	-1,5
W-Et15	0,5	16,4	192,0	0,6	0,0	360,0	75,0	1,9	44,4	84,8	7,7	775,6	3,9
W-Et16	1,3	11,7	95,9	0,6	0,0	591,9	93,0	2,4	27,1	61,9	7,4	885,7	-12,0
W-Et17	0,9	12,9	136,0	0,6	<b>48,0</b>	360,0	87,0	2,3	31,6	67,5	7,5	746,8	-0,2
W-Et19	<b>12,7</b>	32,6	<b>517,0</b>	0,7	0,0	445,4	144,0	3,7	71,2	<b>186,0</b>	<b>7,2</b>	<b>1413,3</b>	6,3
W-Et20	0,6	32,5	<b>578,0</b>	0,7	<b>48,0</b>	421,0	148,0	3,2	72,1	<b>188,0</b>	<b>7,4</b>	<b>1492,2</b>	2,9
<b>Max</b>	12,7	143,0	578,0	0,8	351,0	677,3	148,0	6,6	197,0	188,0	8,6	1492,2	12,3
<b>Min</b>	0,3	4,4	3,9	0,0	0,0	256,3	6,4	0,5	9,7	11,8	7,2	590,0	-12,0
<b>Average</b>	1,3	40,0	147,8	0,5	59,1	448,1	76,8	1,9	73,7	73,8	7,9	923,0	4,2
<b>Stdev</b>	3,0	35,5	175,0	0,3	84,7	139,4	57,3	1,7	54,5	49,7	0,5	269,0	5,8
<b>Skew</b>	3,9	1,9	1,7	-1,4	3,0	0,5	-0,1	1,6	1,0	1,5	0,1	1,1	-1,3

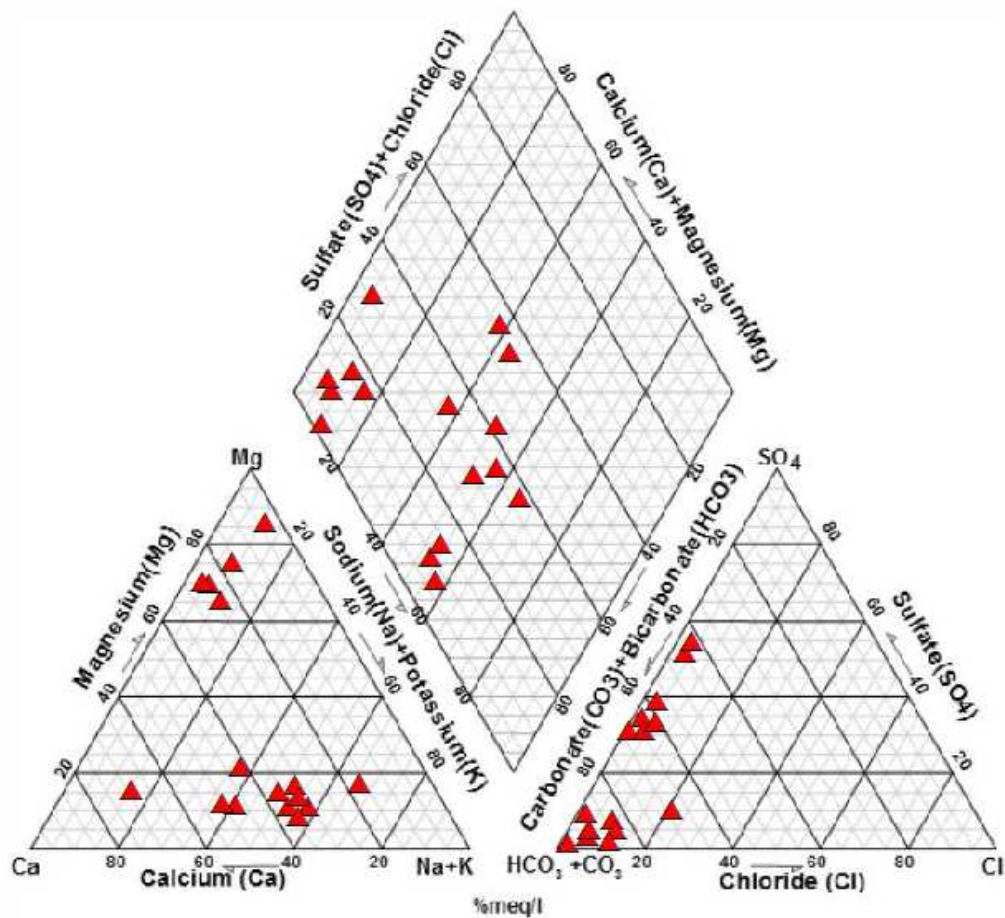
The electron balance of major ions in water sample analysis (table 3) shows that except some of sample stations, it is in the rage of acceptable deviations which is below 5%(Appelo and Postma, 2005). All major ions of show an asymmetric distribution, except Br& Na all are skewed to the right. This can indicate that in some of the ground water samples there is relatively higher concentration of major ions (unusual recordings from the normal distribution).

Water sample number W-et-19 &20 shows a much higher significance amount of total dissolved substances as compared to other water samples. Especially the concentration of Ca and SO<sub>4</sub> in these water samples shows significantly high concentrations as compared with other sample stations. All pH are above 7 which indicates an alkaline type of water and also the pH in sample number W-et-19 &20 is relatively low as compared to other stations. Sample station W-Et 10, W-Et 11 and W-Et 1 shows a highly significant amount of bicarbonate concentrations than other water sample stations. And among the measured major ions bicarbonate ion is the major ion in all sample stations. There are also unusual recordings of chlorine at sample no W-Et 6 and fluorine at W-Et19.

The concentration of total dissolved substance in the study area (table 3) is much higher than that of the standard limit set by WHO (WHO, 2011) which is excellent, less than 300 mg/l; good, between 300 and 600 mg/l; fair, between 600 and 900 mg/l; poor, between 900 and 1200 mg/l; and unacceptable, greater than 1200 mg/l. Water samples stations at W-ET6, W-Et19 and W-Et20 are at the range of unacceptable limit. The high concentration of dissolved solids by itself is not usually a health hazard but with other contaminants could cause diseases (OME, 2003). A high concentration of TDS is an indicator of toxic elements can be present in the water. The positively skewed distribution of most of the major ions (table 3) shows that some of drinking water in study area has unusual elevated concentrations(Carranza, 2008b).

The pH of the study area is neutral to alkaline type and it is in the range of acceptable limit (6.5-8.5) of WHO guidelines for drinking water quality (WHO, 2011), which is all in the desirable ranges. Like TDS, pH usually has no direct impact on human health (Jamshidzadeh and Mirbagheri, 2011).The lowest pH recordings 7.2 and 7.4 at W-Et19 and W-Et20 are highly related with an elevated concentration of total dissolved substances. This is indicating that pH also controls the dissolution of elements and acidic water is synergistic to increased concentration of certain substances(OME, 2003, Fowler et al., 2011).

There are elevated recordings of sulfate concentrations in the study area at sample station W-Et19 and W-Et20 which are 517.0 and 578 mg/l respectively at which the maximum value of sulfate in drinking water is 400 mg/liter (WHO, 2011).. The other sample showed below the limit of values prescribed by WHO. The high concentration of sulfate in water might indicate the sulfate mineral in the aquifer of the system.

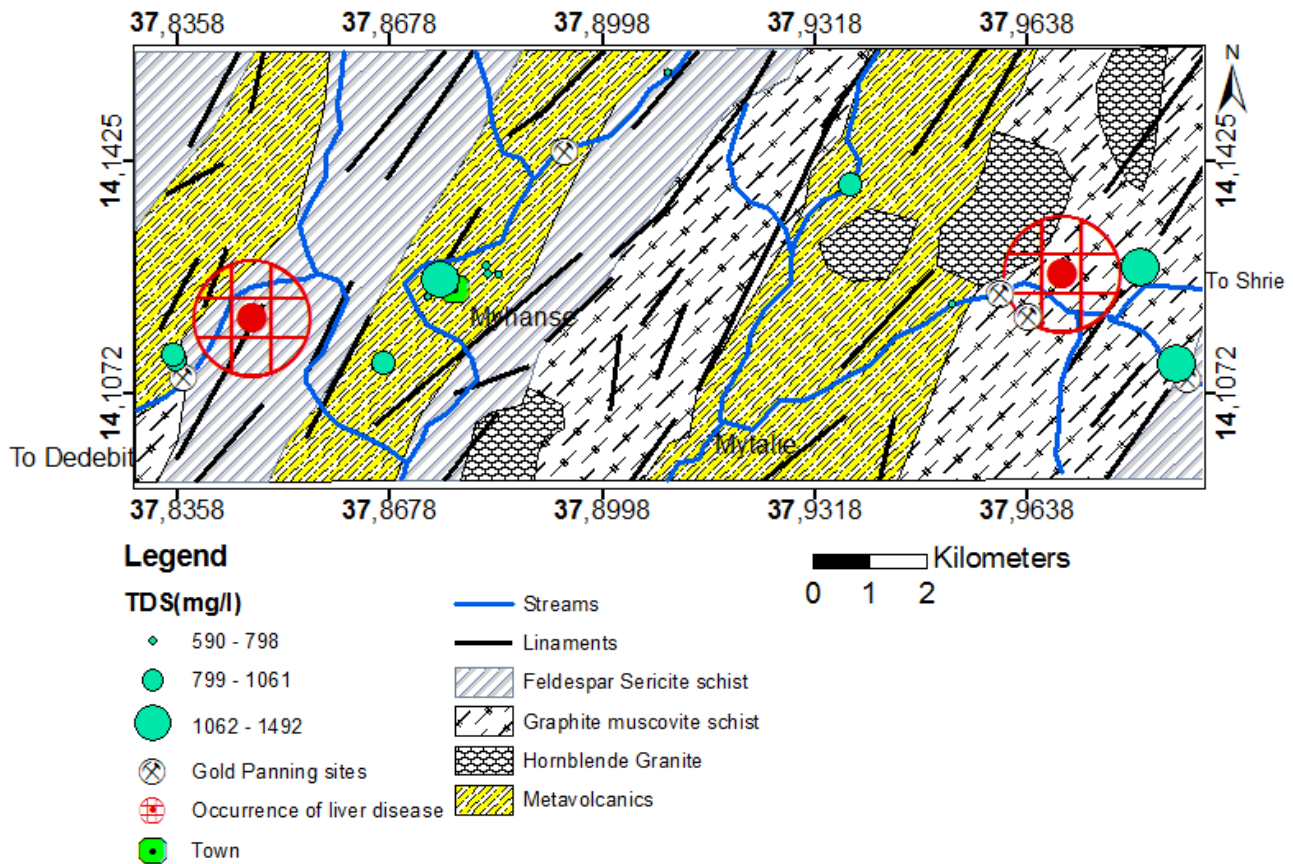


**Figure 12** piper diagram showing distribution of composition major ions in water samples

The piper diagram above (fig 12) shows the type of water in the study area is mainly calcium bicarbonate to intermediate type of water (Fetter and Fetter, 1994). Carbonate type of water are a characteristic of typical of fresh shallow ground water. Some of the water sample shows a significant concentration of magnesium and calcium besides with high bicarbonate ions. The high concentration of calcium and magnesium might be cause for hard water in some of the sample stations.

### 5.1.1 Spatial association of total dissolved substances with lithology





**Figure 13** Distribution of concentration of total dissolved substance (TDS) in water sample of the study area.

Spatially, the elevated concentrations of total dissolved substances are mainly associated with graphite muscovite schist rocks at the western part of the study area (fig 13). There is also high concentration of total dissolved substances with metavolcanic rocks on metavolcanic rocks at the eastern part of some of water sample stations. This elevated TDS concentrations are also related with a high concentration of calcium and sulfate ions as compared to other sample stations (fig 12 and table3). The high spatial association of total dissolved substance on graphite schist rock also shows proximity with liver disease incidence areas in the eastern part of the study area.



## 6.1.2 Bivariate relationship between concentrations of major ions in water samples

The bivariate relationships between concentrations of major ions, with TDS and pH in water sample of the study area are presented below in a correlation matrix

**Table 4** Correlation between major ions (untransformed data), pH and TDS in water sample analysis (with  $\alpha = 0.05$  and  $r$  critical = 0.514)

	<b>F</b>	<b>Cl</b>	<b>SO<sub>4</sub></b>	<b>Br</b>	<b>NO<sub>3</sub></b>	<b>HCO<sub>3</sub></b>	<b>Na</b>	<b>K</b>	<b>Mg</b>	<b>Ca</b>	<b>pH</b>	<b>TDS</b>
F	1											
Cl	-0,08	1,00										
SO <sub>4</sub>	<b>0,58</b>	-0,26	1,00									
Br	0,18	0,33	0,10	1,00								
NO <sub>3</sub>	-0,22	<b>0,70</b>	-0,16	0,36	1,00							
HCO <sub>3</sub>	0,00	0,34	-0,37	0,07	-0,20	1,00						
Na	0,37	-0,20	<b>0,61</b>	-0,43	-0,45	0,01	1,00					
K	0,28	-0,12	0,25	0,34	-0,14	0,05	-0,05	1,00				
Mg	-0,07	0,46	-0,19	0,42	<b>0,65</b>	0,17	<b>-0,61</b>	0,19	1,00			
Ca	<b>0,62</b>	0,08	<b>0,86</b>	0,20	-0,17	0,02	<b>0,67</b>	0,25	-0,19	1,00		
Ph	-0,45	0,24	-0,54	0,02	<b>0,52</b>	-0,18	<b>-0,73</b>	0,00	0,50	<b>-0,71</b>	1,00	
TDS	0,49	0,43	<b>0,63</b>	0,29	0,20	0,31	0,45	0,21	0,27	<b>0,83</b>	-0,44	1,00

The correlation matrix above (table 4) using the raw data analysis shows a strong positive correlation between Ca and SO<sub>4</sub> and there is also significant positive correlation between Ca & F, Ca & Na, SO<sub>4</sub> & Na, NO<sub>3</sub> & Cl and Mg & NO<sub>3</sub>. There is also a significance negative correlation between Mg & Na. The rest of other correlations between ions are not significant. The pH of water sample is mainly positively correlated with HCO<sub>3</sub> concentrations and negatively correlated with Na and Ca.

Despite the type of water shown in piper diagram (fig 12) which is more of carbonate type of water; the variability of total dissolved substances is highly and positively correlated with the concentration of calcium and sulfate ions. And there is a significant association of calcium and sulphate ions. Carbonate ion does not show any significant association with other major ions. Lack of significant correlation between bicarbonate ions and calcium and magnesium ions indicates they are from different source (Singh and Hasnain, 1998). And it also indicates

that the type of water in the study area is not a calcium carbonate type of water that can source from limestone and dolomite containing aquifers (Appelo and Postma, 2005). The elevated concentration of bicarbonate ion also does not show association with the graphite schist rocks (table 3). Therefore the dominant major bicarbonate ions in the water samples of the study area might be dissolved from the unknown carbon containing compounds that are observed in XRD analysis of rock and soil samples (table 1) and/or dissolution of atmospheric CO<sub>2</sub>. The negative correlation of magnesium and sodium also indicates they are dissolved from different type of minerals.

## **6.2 Trace elements in water samples and cause of liver disease in the study area**

Among trace elements that cause liver disease (As, Pb, Se, Tm, Br, Ni, Cr, Cu, Al, F, Cd, Mg, Ag, Au, Mn, Mo, Co, Tl, Zn, V and Hg) only Au is not measured and among the measured trace elements all or most of measured concentrations of Ag, Hg, Cr, Al, Cd, Tm, Se, and Tl are below detection limit (table 5). The distribution of these element analysis, except Tm, Br & Mg shows an asymmetric distribution which is skewed to the right. This also indicates that there is relatively higher concentration of these elements in some of the water sample stations. Except Co, Fe and Mg the maximum tolerable limit (MTL) in ground water is set, and at some sample stations the concentration of As, F, Pb, Zn and Br are above or around MTL. Like total dissolved substances, water sample number W-et-19 & 20, which are on graphite schist rock (fig 7), also shows a significance amount of concentrations above MTL of these elements (F, Pb, Zn and Br) as compared to other water samples. Sample station W-Et 1 and W-Et 5 shows a significantly high concentration of arsenic (above MTL) than other sample stations. The concentration of bromide element is above MTL in most of the sample stations. The elevated concentration of Zn and Pb are observed at W-Et20 which has also showed high TDS concentration and pH. pH is more crucial parameter for metal mobility (Grybos et al., 2007).

Based on the maximum tolerable limit set by WHO; As, F, Pb, Zn and Br are the probable geochemical pollutants that could cause the liver disease incidence in the study area. Exposures to these elements occur as mixtures (Fowler et al., 2011), and is important to consider interactions among these elements. The interaction between these different substances may result to detoxifying, additive or synergetic effect (Selinus, 2005, Duruibe et

al., 2007, WHO, 2011). Therefore the incidence of liver disease in the study area might be caused by the interaction of elements whose concentration is above MTL by the additive or synergetic effects. The MTL guideline value for Fe, Co, and Mg is not determined and these elements can also cause or contribute the incidence of this liver disease.

**Table 5** The analytical results and summery statistics of elements (trace and major elements that cause liver disease) in the water samples. (All are in ppb, MTL= maximum tolerable limit)

S.No	Ag	Al	As	Cd	Co	Cr	Cu	Fe	F	Hg	Mg	Mn	Mo	Ni	Pb	Se	Tl	Tm	Zn	Br	V
W-Et1	<0,6	<6	<b>75,9</b>	0,03	0,21	<1,5	2,4	30	<b>3780</b>	<0,6	>60000	0,3	0,6	1,5	0,3	1,8	0,006	<0,003	8,1	<b>590</b>	7,8
W-Et2	<0,6	9	<b>9,99</b>	0,03	0,36	<1,5	4,5	<30	<b>4920</b>	<0,6	>60000	0,9	0,6	8,7	1,17	<0,6	0,015	<0,003	12,9	<b>590</b>	6
W-Et3	<0,6	<6	1,44	<0,03	0,06	2,1	1,8	30	450	<0,6	>60000	0,6	<0,3	<0,9	0,27	<0,6	0,003	<0,003	7,5	<b>520</b>	0,2
W-Et4	<0,6	<6	9,3	<0,03	0,57	<1,5	3	<30	810	<0,6	>60000	0,3	0,3	5,4	0,15	0,6	<0,003	<0,003	12,3	<b>580</b>	6,5
W-Et5	<0,6	6	<b>10,32</b>	0,18	0,45	<1,5	3,9	30	750	<0,6	>60000	0,6	0,6	7,5	0,42	0,9	0,006	<0,003	14,1	<b>580</b>	8,1
W-Et6	<0,6	<6	2,49	<0,03	0,15	<1,5	2,1	30	450	<0,6	>60000	0,6	0,6	1,2	0,21	<0,6	0,006	<0,003	9,6	<b>810</b>	4,7
W-Et7	<0,6	12	0,27	0,15	0,12	<1,5	1,8	30	690	<0,6	18810	0,6	0,6	<0,9	0,24	0,6	0,003	<0,003	9,3	<10	0,9
W-Et8	<0,6	<6	<0,09	<0,03	0,12	<1,5	1,8	30	450	<0,6	27660	0,3	0,3	<0,9	0,3	<0,6	0,003	<0,003	6,9	<10	4
W-Et9	<0,6	<6	0,09	<0,03	0,39	<1,5	1,8	30	900	<0,6	48900	0,3	0,9	<0,9	0,15	<0,6	0,003	<0,003	7,5	<b>610</b>	1,4
W-Et10	<0,6	<6	0,42	<0,03	0,12	<1,5	1,8	30	420	<0,6	15210	0,9	<0,3	0,9	0,51	<0,6	<0,003	<0,003	10,8	<10	0,3
W-Et11	<0,6	<6	0,33	<0,03	0,12	<1,5	1,5	60	570	<0,6	14340	6,9	0,3	0,9	0,27	<0,6	<0,003	<0,003	6,3	<b>520</b>	0,5
W-Et15	<0,6	<6	1,11	<0,03	0,12	<1,5	1,8	30	1380	<0,6	27630	0,6	1,8	<0,9	0,27	0,6	0,003	<0,003	12	<b>590</b>	1
W-Et16	<0,6	<6	0,51	0,03	0,15	<1,5	1,8	60	<b>2190</b>	<0,6	17130	1,2	2,7	<0,9	0,3	<0,6	<0,003	<0,003	12	<b>580</b>	1,2
W-Et17	<0,6	<6	0,87	0,03	0,09	<1,5	2,1	30	<b>1980</b>	<0,6	24480	0,6	3,9	<0,9	0,18	<0,6	0,003	<0,003	10,2	<b>590</b>	1,6
W-Et19	<0,6	<6	0,36	0,03	0,15	<1,5	-2,1	30	<b>2370</b>	<0,6	53700	8,7	4,5	<0,9	0,15	<0,6	<0,003	<0,003	8,7	<b>670</b>	0,3
W-Et20	<0,6	111	1,2	0,12	0,3	<1,5	12	90	<b>2190</b>	<0,6	46200	4,2	4,8	1,8	<b>9,03</b>	<0,6	0,003	<0,003	<b>48,9</b>	<b>680</b>	0,6
<b>MTL</b>	10	200	<b>10</b>	3	...	50	2000	...	<b>1500</b>	6	..	400	10	70	<b>10</b>	40	0.5	2	<b>50</b>	<b>10</b>	50
<b>Max</b>	<0,6	111	<b>75,9</b>	0,18	0,57	2,1	12	90	<b>4920</b>	<0,6	>60000	8,7	4,8	8,7	<b>9,03</b>	1,8	0,015	<0,003	<b>48,9</b>	<b>810</b>	8,1
<b>Min</b>	<0,6	<6	<0,09	<0,03	0,06	<1,5	1,5	<30	420	<0,6	14340	0,3	0,3	<0,9	0,15	<0,6	<0,003	<0,003	6,3	<10	0,2
<b>Average</b>	0,6	13,5	7,2	0,1	0,2	1,5	2,9	37,5	1518,8	0,6	40878,8	1,7	1,4	2,2	0,9	0,7	0,0	0,0	12,3	496,3	2,8
<b>Stdev</b>	0,0	26,1	18,7	0,0	0,2	0,1	2,6	17,3	1322,5	0,0	19121,0	2,6	1,6	2,6	2,2	0,3	0,0	0,0	10,0	250,6	2,9
<b>Skew</b>	1,1	4,0	3,7	2,0	1,2	4,0	3,4	2,4	1,5	1,1	-0,3	2,1	1,3	1,9	3,9	3,7	3,1	-1,1	3,6	-1,4	0,8

### 6.2.1 Bivariate relationship between concentrations of trace elements in water samples.

The bivariate relationship between elements of trace elements and some major ions both untransformed (row) data are presented below.

**Table 6** Correlation between trace elements, in water sample on row data (with  $\alpha = 0.05$  and  $r_{critical} = 0.514$ )

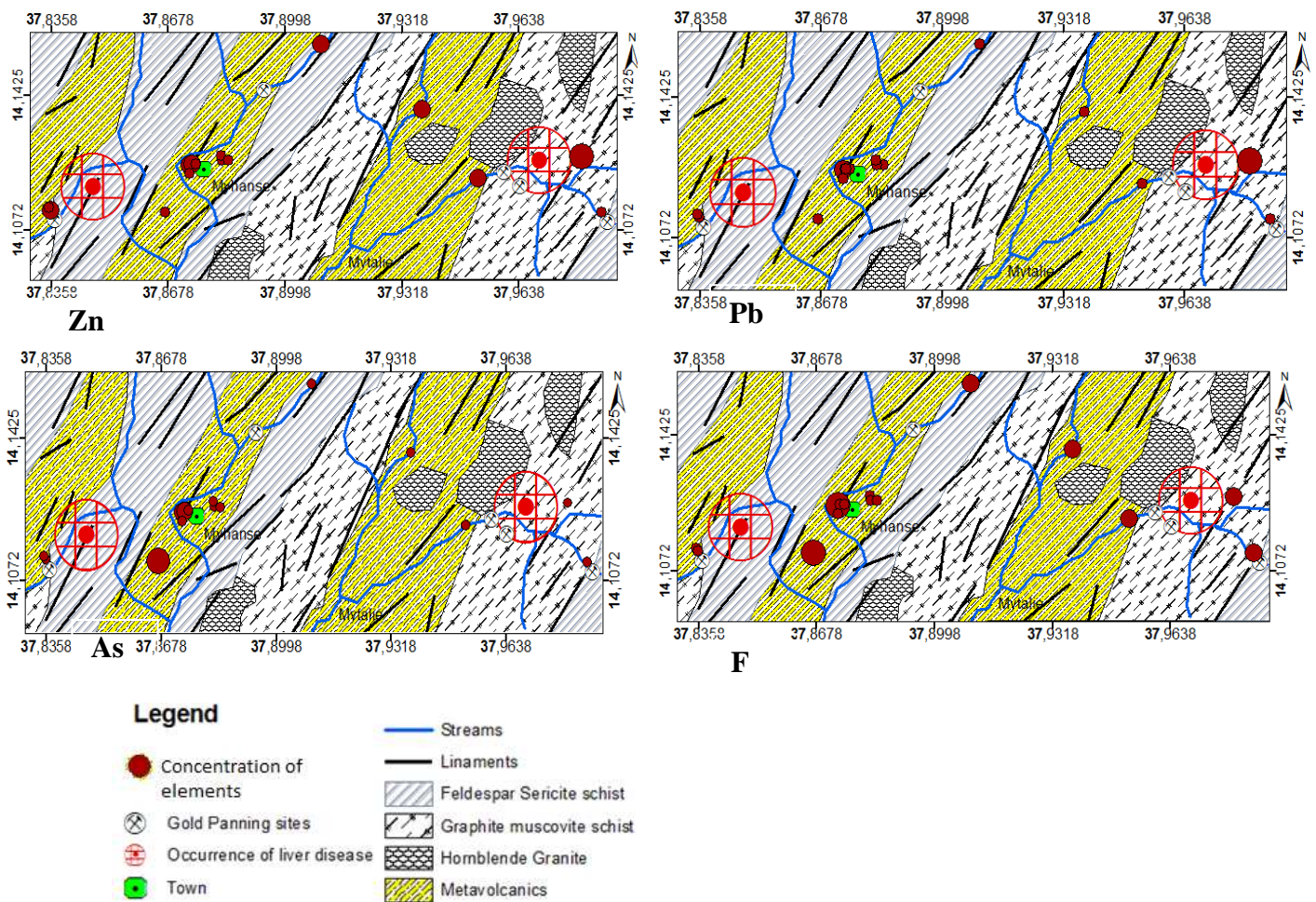
	<i>As</i>	<i>Co</i>	<i>Cu</i>	<i>Fe</i>	<i>F</i>	<i>Mg</i>	<i>Mn</i>	<i>Mo</i>	<i>Pb</i>	<i>Zn</i>	<i>Br</i>	<i>V</i>	<i>SO4</i>
As	1,00												
Co	0,14	1,00											
Cu	-0,01	0,36	1,00										
Fe	-0,16	0,00	<b>0,71</b>	1,00									
F	0,51	0,16	0,30	0,09	1,00								
Mg	0,38	<b>0,56</b>	0,26	-0,24	0,30	1,00							
Mn	-0,20	-0,18	0,18	0,43	0,09	-0,10	1,00						
Mo	-0,20	-0,14	0,49	0,49	0,32	-0,08	0,50	1,00					
Pb	-0,08	0,17	<b>0,97</b>	<b>0,80</b>	0,20	0,09	0,24	<b>0,53</b>	1,00				
Zn	-0,10	0,26	<b>0,97</b>	<b>0,77</b>	0,19	0,11	0,18	<b>0,56</b>	<b>0,98</b>	1,00			
Br	0,15	0,31	0,27	0,22	0,36	<b>0,58</b>	0,23	0,39	0,19	0,23	1,00		
V	<b>0,61</b>	<b>0,61</b>	0,04	-0,34	0,30	<b>0,60</b>	-0,42	-0,41	-0,17	-0,11	0,20	1,00	
SO4	-0,27	-0,07	<b>0,55</b>	0,45	0,11	-0,02	<b>0,55</b>	<b>0,78</b>	<b>0,62</b>	<b>0,59</b>	0,10	-0,41	1,00
NO3	-0,01	0,18	0,03	-0,19	-0,11	0,46	-0,29	-0,22	-0,04	-0,02	0,36	0,37	-0,16

On row data correlation analysis between trace elements (table 6) there is a positive strong, almost linear, association between Zn, & Pb, and Zn & Cu . There is also significant positive correlation between Cu &Fe, Mg &Co, Pb & Mo, Zn & F, Zn & Mo, Br & Ma, V & As, V & Co, and V & Mg. Sulfate ion shows a significant correlation with Mn, Mo, Pb, and Zn.

Among those elements at which their concentration are above MTL (As, F, Pb, Zn and Br), the strong association of Pb and Zn suggested that there could be a great contribution to the additive effect in the incidence of this liver disease from these two elements. Both Pb and Zn also show a strong association with Cu and SO<sub>4</sub> which could indicate the similarity of source rock like sulfide minerals and, or their similarity in dissolution characteristics. A given element in water can be existed in different specious (Carroll. et al.), forexample Zn is present as simple hydrated metal ion (e.g., Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup>), simple inorganic complexes (e.g., Zn(H<sub>2</sub>O)<sub>5</sub>Cl<sup>+</sup>), simple organic complexes (e.g., Zn-citrate), stable inorganic complexes (e.g.,

ZnS), stable organic complexes(e.g., Zn-humate), adsorbed on inorganic colloids (e.g., Zn+2Fe<sub>2</sub>O<sub>3</sub>), and adsorbed on organic colloids (e.g., Zn+2-humic acid). And all these species of zinc have different level of toxicity to human body. Therefore besides to the additive and synergetic effect, the different speciation of elements determines the toxicity of a substance (Fowler, 2011).

### 6.2.2 Spatial association of element concentration in ground water with lithology and liver disease occurrence areas.



**Figure 14** Spatial association of As, Pb, Zn and F with lithology

The anomalous concentration of zinc and lead shows a strong spatial association with liver disease incidence areas at Eastern part of the study area (fig 14) which is on graphite muscovite schist rocks. There is also a spatial association of arsenic and fluorine in water samples

with metavolcanic rocks on some of sample stations at western part of the study area. At wells sites at which a dense population used to drink, around myhanse village, only shows high concentration of fluorine as compared to other well sites. At liver incidence site on western part of the study area, among the two water source wells one of them shows anomalous concentration of Arsenic. This could be a probable cause this liver disease on this part of the study area besides to additive and synergetic effect of other elements.

In order to understand the relationship between lithology of the area and elements (at which their concentration in water sample is above maximum tolerable limit), box plots were created using R statistics shown below (fig 15). The box plot indicates that there is a clear relationship of association between the graphite muscovite schist rocks with concentrations of Lead, zinc and bromide in the study area. The number of observations (water samples) on graphite muscovite schist rock is small (there are only two) as compared to metavolcanic (seven) and feldspar sericite schist (three) rocks which makes that it is not confidential to trust this relationship to produce reliable conclusion. And also arsenic shows a significant association with the metavolcanic rock.

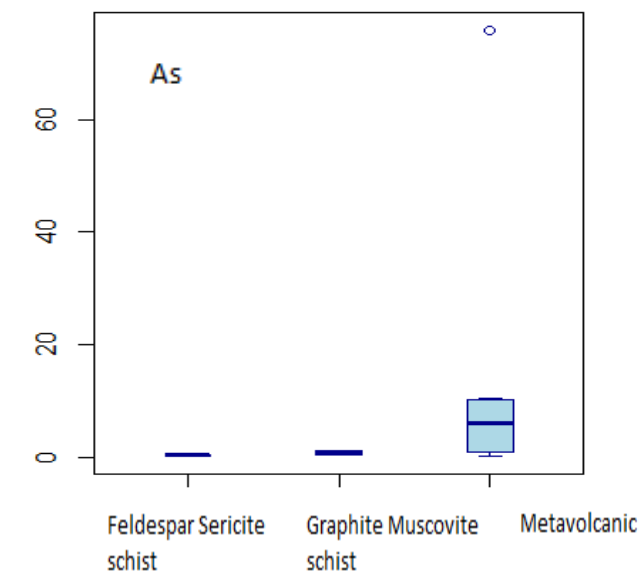
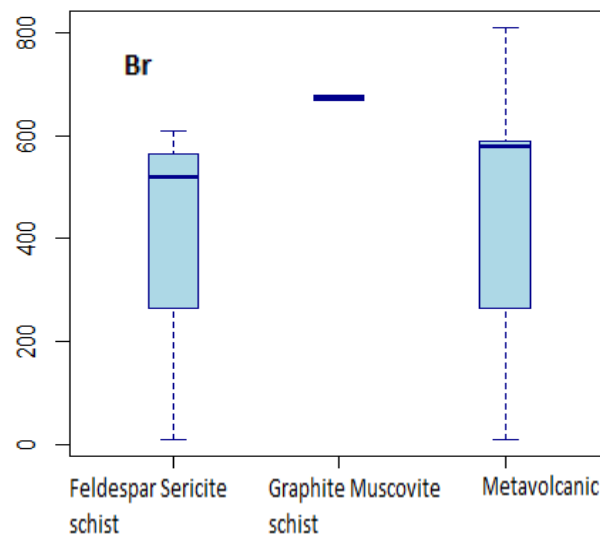
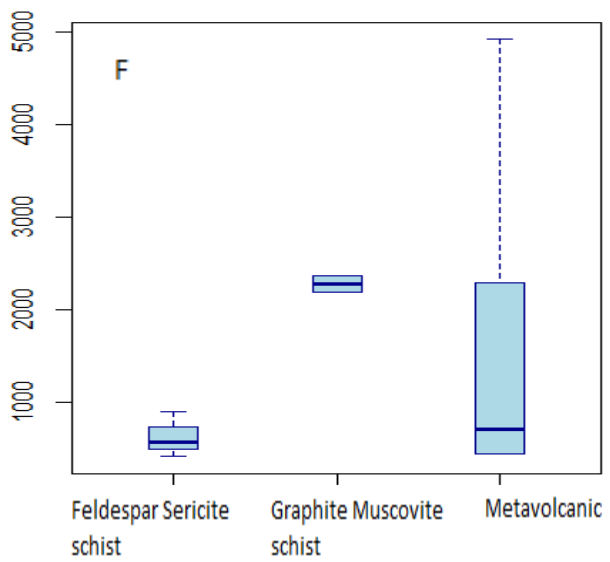
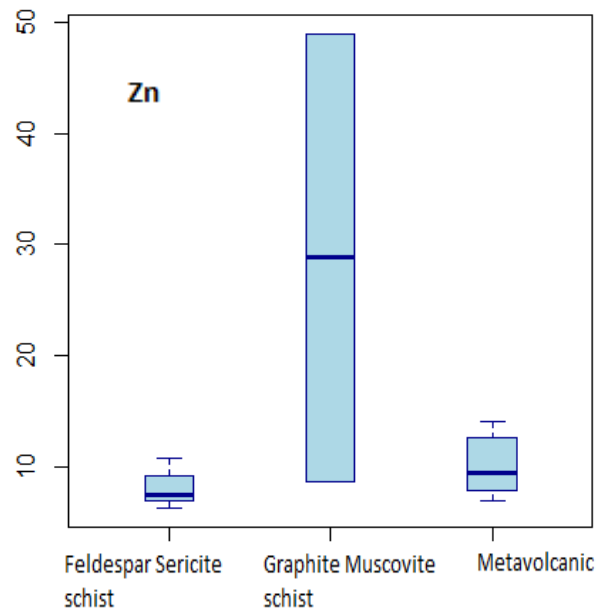
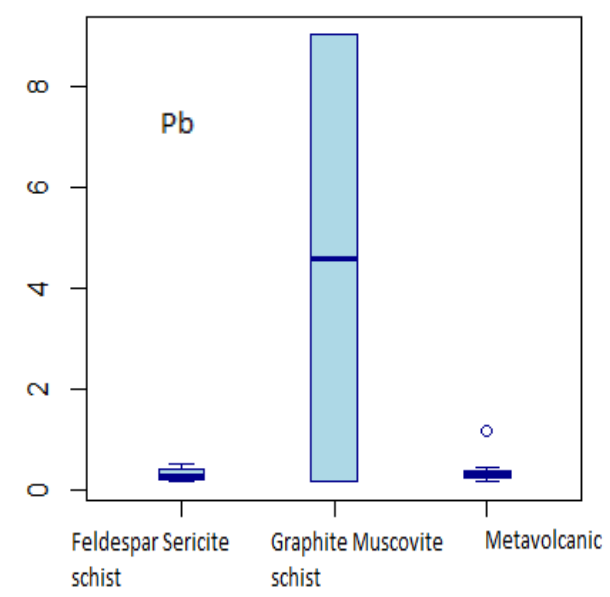


Figure 15 Box plot between element concentrations in water samples of those elements having above maximum tolerable limit with lithology identified in respective sampling site.



### 6.3 Trace elements in rock samples

**Table 7** The analytical results and summery statistics of trace elements in rock samples (selected elements that cause liver disease) (all are in ppm).

S.No	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Ni	Pb	Zn	Tl	S
R-Et1	< 0.2	62100	5	< 0.5	39	105	55	73900	<1	35200	912	1	87	< 2	76	<2	<b>200</b>
R-Et2	< 0.2	31900	<b>28</b>	< 0.5	27	62	173	42800	<1	11500	1350	<1	18	<b>43</b>	71	<2	<100
R-Et3	< 0.2	1600	3	< 0.5	103	1000	2	84600	<1	208000	936	<1	2050	< 2	10	<2	<100
R-Et4	< 0.2	4500	3	< 0.5	119	1660	9	92900	<1	199000	1150	<1	1300	< 2	32	<2	<100
R-Et5	< 0.2	12100	<b>20</b>	< 0.5	19	95	74	47100	<1	1400	945	2	49	5	86	<2	<100
R-Et8	< 0.2	200	2	< 0.5	2	503	8	6200	<1	600	76	5	24	< 2	3	<2	<100
R-Et9	< 0.2	49800	2	< 0.5	40	328	5	93900	<1	21900	746	<1	158	< 2	104	<2	<100
R-Et10	< 0.2	26900	11	< 0.5	30	131	58	45100	<1	2900	818	3	71	2	81	<2	<100
R-Et11	< 0.2	5100	2	< 0.5	<1	59	2	5800	<1	500	173	<1	4	<b>27</b>	14	<2	<100
R-Et11-2	< 0.2	14800	2	< 0.5	3	60	26	62400	<1	1400	3580	3	6	2	196	<2	<100
R-Et13	< 0.2	51500	4	< 0.5	39	400	13	91600	<1	20600	839	<1	168	< 2	101	<2	<100
R-Et18	< 0.2	300	2	< 0.5	2	534	9	5800	<1	200	39	5	24	< 2	< 2	<2	<100
R-Et19	< 0.2	19500	2	< 0.5	2	93	39	22200	<1	9400	727	2	12	4	92	<2	<b>300</b>
R-Et20	< 0.2	16300	2	< 0.5	2	32	43	19700	<1	8800	583	1	8	6	86	<2	<b>300</b>
Max	< 0.2	62100	28,0	< 0.5	119,0	1660,0	173,0	93900,0	<1	208000	3580,0	5,0	2050,0	43	196,0	<2	300
Min	< 0.2	200,0	2,0	<0.5	<1	32,0	2,0	5800,0	<1	200	39,0	<1	4,0	<2	<2	<2	<100
Average	< 0.2	21185,7	6,3	<0.5!	32,8	361,6	36,9	49571,4	<1	37242,9	919,6	2,0	284,2	12,7	73,2	<2	266,7
Stdev	..	20581,1	8,0	...	38,1	463,2	45,8	33989,4	...	71198,9	857,5	1,5	609,6	16,0	51,4	....	...
Skew	..	0,9	2,1	..	1,5	2,1	2,2	0,0	...	2,2	2,4	1,4	2,5	1,5	0,8	...	...

The analysis result of trace elements on rock samples listed in the above table (table 7) shows that some elements at the entire sample or at some sample stations (Ag, Cd, Hg, Tl &S) are below detection limit. The distribution of all of element analysis in this rock samples (except Fe which is normally distributed) shows an asymmetric distribution which is skewed to the right. This also indicates that, like the distribution of elements in water, in some parts of the rock sample stations there is relatively higher concentration of such elements. Sample station R-et-19 &20 shows a much significant concentration of sulfur as compared to other sample stations. But this sample stations does not show a significant anomalous concentration of other elements as compared with concentration in water samples (table3 and table 7).

The high concentration of; sulfur (table 7), Polar organic compounds (table 2) in the rock samples and sulfate ion concentration in water solution (table 3) indicates that this graphite schist type of rock in the study have sulfur related minerals which contain trace elements in the form of organic sulfide minerals. This type of rocks form under reduced environment in the process of metamorphism (Frost, 1988, Nesbitt, 1980). Therefore the oxidation of this rock in aqueous system could result in the release of trace elements into the aquifer.

**Table 8** Bivariate correlation between trace elements in rock sample analysis on row data (with  $\alpha = 0.05$  and  $r$  critical = 0.532)

	<i>Al</i>	<i>As</i>	<i>Co</i>	<i>Cu</i>	<i>Fe</i>	<i>Cr</i>	<i>Mg</i>	<i>Mn</i>	<i>Mo</i>	<i>Pb</i>	<i>Zn</i>	<i>Sr</i>	<i>V</i>
<i>Al</i>	1,00												
<i>As</i>	0,15	1,00											
<i>Co</i>	0,01	-0,03	1,00										
<i>Cu</i>	0,27	<b>0,91</b>	-0,16	1,00									
<i>Fe</i>	0,52	-0,01	<b>0,75</b>	-0,09	1,00								
<i>Cr</i>	-0,36	-0,28	<b>0,83</b>	-0,42	0,44	1,00							
<i>Mg</i>	-0,25	-0,18	<b>0,94</b>	-0,27	<b>0,57</b>	<b>0,87</b>	1,00						
<i>Mn</i>	0,11	0,12	0,07	0,20	0,41	-0,09	0,06	1,00					
<i>Mo</i>	-0,46	-0,16	-0,45	-0,19	<b>-0,56</b>	-0,04	-0,37	-0,12	1,00				
<i>Pb</i>	0,00	<b>0,63</b>	-0,18	<b>0,67</b>	-0,29	-0,31	-0,20	-0,02	-0,30	1,00			
<i>Zn</i>	0,47	0,09	-0,24	0,22	0,34	-0,47	-0,35	<b>0,79</b>	-0,20	-0,13	1,00		
<i>Sr</i>	<b>0,89</b>	-0,16	-0,09	0,04	0,39	-0,36	-0,23	0,07	-0,45	-0,15	0,44	1,00	
<i>V</i>	<b>0,93</b>	0,18	0,24	0,20	<b>0,66</b>	-0,11	-0,05	0,00	-0,50	-0,08	0,35	<b>0,74</b>	1,00
<i>S</i>	0,14	-0,24	-0,29	0,08	-0,27	-0,32	-0,17	-0,13	-0,21	-0,13	0,18	0,41	-0,02

Correlation analysis on the untransformed data of rock sample (table 8) indicates that there is a strong positive correlation between Cu & As, V & Al, Al & Sr, Cr & Co, and Mg, & Co. Because of the measurement of sulphur concentration on most of sample station is below detection limit, it does not show a significant correlation with other trace elements.

There is much significant difference in bivariate correlation between elements that are observed in bivariate analysis of trace elements in water samples (table 6) and in rock samples (table 8). This difference might come due to selective geochemical dispersion mechanisms (White, 2013, Fowler et al., 2011). During the crystallization of rocks from the cooling of rock melt, the major constituents form a sequence of minerals dependent on the prevailing temperature, pressure and pH conditions and the individual trace elements incorporated into particular coordination sites where concentrations rarely vary by more than a factor of two, over a wide range of geological formations. And during another dispersion process, there could be a selective redistribution of chemical elements which involves interactions between bedrock and water from atmospheric precipitations or from the aquifer. Such process might be responsible for the variability of the distribution of trace elements in rock samples and water samples in the study area. Another reason for this lack of patterns between the rock and soil might be because of the movement of pollutants in the aquifer. The type of aquifer in the study area is fractured aquifers which have a high degree of transitivity (Mayer, 1998).

## 6.4 Trace elements in soil samples

**Table 9** The analytical results and summery statistics of trace elements in soil (with code S) and stream sediment ( SS) samples (selected elements that cause liver disease) (all are in ppm),

S.no	Ag	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mg	Mn	Mo	Ni	Pb	Zn	Tl	S
S-Et1	< 0.2	67000	18	< 0.5	44	161	103	81900	<1	22700	2000	< 1	87	<2	74	1400	<100
SS-Et1	< 0.2	43400	<b>31</b>	< 0.5	37	422	65	71000	<1	<b>31200</b>	1050	< 1	172	<2	76	1300	<100
S-Et8	< 0.2	48000	<2	< 0.5	41	285	68	64000	<1	19900	1580	< 1	103	3	71	1300	<100
SS-Et8	< 0.2	32200	11	< 0.5	34	137	92	66200	<1	14400	1490	< 1	63	6	93	1700	<100
S-Et10	< 0.2	52000	12	< 0.5	19	69	129	53900	<1	13000	260	< 1	31	6	74	1200	<100
SS-Et10	< 0.2	26200	9	< 0.5	23	124	60	58100	<1	9500	1040	1	23	6	62	500	<100
S-Et11	< 0.2	23500	4	< 0.5	19	79	63	45300	<1	6500	773	< 1	23	5	62	300	1300
SS-Et11	< 0.2	27400	11	< 0.5	22	89	57	49600	<1	7200	1080	< 1	19	8	54	1000	<100
S-Et12	< 0.2	23600	7	< 0.5	23	97	56	54800	<1	9300	1020	< 1	20	8	63	400	<100
S-Et13	< 0.2	51100	11	< 0.5	29	132	61	65400	<1	7700	1260	< 1	32	3	68	1800	200
S-Et14	< 0.2	39000	6	< 0.5	19	68	79	46100	<1	5200	1110	< 1	12	6	43	800	<100
SS-Et15	< 0.2	18000	3	< 0.5	3	56	29	69500	<1	1700	3300	3	6	3	<b>230</b>	100	<100
SS-Et16	< 0.2	27100	6	< 0.5	21	166	85	52800	<1	11400	850	1	53	5	92	2200	200
SS-Et17	< 0.2	8500	<2	< 0.5	7	153	17	23500	<1	2500	459	2	15	2	24	1000	<100
S-Et18	< 0.2	52800	2	< 0.5	18	97	48	48100	<1	12200	748	1	38	5	69	2400	100
S-Et19	< 0.2	23700	2	< 0.5	16	218	55	43300	<1	9600	986	3	31	5	57	1300	100
Max	< 0.3	67000	31	< 0.5	44	422	129	81900	<1	31200	3300	3	172	8	230	2400	1300
Min	< 0.4	8500	<2	< 0.5	3	56	17	23500	<1	1700	260	<1	6	<2	24	100	<100
Average	< 0.5	35218,8	9,5	< 0.5	23,4	147,1	66,7	55843,8	<1	11500,0	1187,9	1,8	45,5	5,1	75,8	1168,8	...
Stdev	...	15770,1	7,7	...	11,2	94,8	27,1	13875,6	<1	7669,7	701,0	...	43,2	1,8	44,4	658,0	...
Skew	...	0,4	1,8	...	0,2	1,9	0,5	-0,4	<1	1,3	1,9	...	2,0	0,0	3,0	0,2	...

Trace element concentration analyses in soil and stream sediment (table 9) all except iron are positively skewed. In all or parts of the sample, concentration of Ag, Cd, Hg, S and Mo are below detection limit. There is no much significant elevated concentration recorded within all soil sample analysis. But there is an anomaly recording of arsenic and magnesium at stream sediment of SS-Et1 as compared to soil samples. This could indicate that some geochemical pollutants might accumulate at stream sediment samples during dispersion process. And this could be a health risk at which the local people used to pan for gold which increases the exposure of local people to stream sediment pollutants than soil related pollutants. At most of the sample stations, concentrations of arsenic in soil and stream sediment samples are higher than in rock samples (table 7&9). This could be because of selective mobility of geochemical elements during dispersion. The dispersion might be through natural process like weathering and dissolution (Fowler, 2011) or the anthropogenic effect of artesian mining itself (fig 11).

**Table 10** Correlation between trace elements in soil sample analysis on row data (with  $\alpha = 0.05$  and  $r$  critical = 0.62)

	<i>Al</i>	<i>As</i>	<i>Co</i>	<i>Cu</i>	<i>Fe</i>	<i>Cr</i>	<i>Mg</i>	<i>Mn</i>	<i>Pb</i>	<i>Zn</i>	<i>Sr</i>	<i>V</i>
<i>Al</i>	1,00											
<i>As</i>	0,61	1,00										
<i>Co</i>	0,61	0,47	1,00									
<i>Cu</i>	0,51	<b>0,70</b>	0,23	1,00								
<i>Fe</i>	<b>0,73</b>	<b>0,75</b>	<b>0,92</b>	0,38	1,00							
<i>Cr</i>	0,09	-0,24	0,58	-0,21	0,34	1,00						
<i>Mg</i>	<b>0,67</b>	0,38	<b>0,81</b>	0,39	<b>0,76</b>	0,58	1,00					
<i>Mn</i>	0,38	0,33	<b>0,86</b>	-0,08	<b>0,75</b>	0,58	0,58	1,00				
<i>Pb</i>	-0,65	-0,32	<b>-0,74</b>	-0,11	<b>-0,69</b>	-0,56	-0,60	<b>-0,68</b>	1,00			
<i>Zn</i>	0,58	0,40	0,51	0,33	<b>0,62</b>	0,24	<b>0,70</b>	0,11	-0,44	1,00		
<i>Sr</i>	-0,02	0,12	-0,15	-0,19	-0,05	-0,33	-0,62	0,04	-0,02	-0,47	1,00	
<i>V</i>	<b>0,80</b>	<b>0,69</b>	<b>0,74</b>	0,26	<b>0,87</b>	0,25	0,52	<b>0,70</b>	<b>-0,78</b>	0,40	0,31	1,00

The bivariate association of trace elements in the soil also show not much significant relation with the association showed in water and rock sample analysis. Such difference also could be a result of dispersion process (White, 2013, Fowler, 201188). Through processes of weathering from rocks, diffusion, compaction, erosion and bioturbation, trace metals released into the aquifer system(Förstner, 1980) and also in addition to the physical processes, "biologically mediated reactions occur in the sediment, can form more toxic organo-metallic compounds.

All such process could change the variability of trace elements as compared to the source rock.

## 6.5 Compositional data analysis and bivariate association of elements in water and rock samples.

**Table 11** Correlation between trace elements, major ions which is after a transformation of the data by additive log ratio (alr) method, in water sample analysis (with  $\alpha = 0.05$  and r critical = 0.514)

	<i>As</i>	<i>Co</i>	<i>Cu</i>	<i>Fe</i>	<i>F</i>	<i>Mg</i>	<i>Mn</i>	<i>Mo</i>	<i>Pb</i>	<i>Zn</i>	<i>Br</i>	<i>V</i>	<i>SO4</i>
<b>As</b>	1,00												
<b>Co</b>	0,41	1,00											
<b>Cu</b>	0,41	<b>0,58</b>	1,00										
<b>Fe</b>	-0,15	0,05	0,46	1,00									
<b>F</b>	0,43	0,30	0,43	0,18	1,00								
<b>Mg</b>	<b>0,58</b>	0,51	0,46	-0,30	0,25	1,00							
<b>Mn</b>	-0,24	-0,15	0,21	<b>0,61</b>	0,20	-0,23	1,00						
<b>Mo</b>	-0,12	-0,01	0,33	0,37	<b>0,62</b>	0,01	0,43	1,00					
<b>Pb</b>	<b>0,68</b>	<b>0,77</b>	0,61	-0,10	0,29	<b>0,55</b>	-0,16	-0,19	1,00				
<b>Zn</b>	0,23	0,41	<b>0,90</b>	<b>0,57</b>	0,35	0,18	0,26	0,50	0,38	1,00			
<b>Br</b>	0,38	0,25	0,23	0,18	0,45	0,41	0,19	0,41	0,23	0,19	1,00		
<b>V</b>	<b>0,59</b>	<b>0,61</b>	0,22	-0,29	0,22	0,43	<b>-0,58</b>	-0,22	<b>0,64</b>	0,02	0,11	1,00	
<b>SO4</b>	-0,49	0,09	0,22	0,25	0,27	-0,12	0,27	<b>0,70</b>	-0,26	0,34	0,03	-0,07	1,00
<b>NO3</b>	0,32	0,34	0,37	-0,32	-0,12	<b>0,52</b>	<b>-0,61</b>	-0,31	0,41	0,15	-0,02	0,51	-0,17

The bivariate correlation between trace elements in water after alr transformation of the data (table 13) does not show a strong correlation between Zn& Pb and Zn & Cu as compared to a bivariate correlation analysis on the untransformed data (table 6), only between Zn and Cu shows a significant correlation. And there are new significant correlations like between As & Pb, As & Mg, Pb & Co and V& Pb. Sulfate only have a significant correlation with Mo in this alr transformed data.

**Table 12** Correlation between trace elements after a transformation of the data by centered log ratio (clr) method in water sample analysis (with  $\alpha = 0.05$  and  $r$  critical = 0.514)

	As	Co	Cu	Fe	F	Mg	Mn	Mo	Pb	Zn	Br	V	SO4
As	1,00												
Co	0,08	1,00											
Cu	-0,07	-0,08	1,00										
Fe	<b>-0,57</b>	-0,32	0,08	1,00									
F	0,20	-0,13	-0,05	-0,04	1,00								
Mg	0,29	0,08	-0,29	-0,53	-0,15	1,00							
Mn	-0,41	-0,33	0,19	<b>0,63</b>	0,15	-0,34	1,00						
Mo	-0,38	-0,37	0,10	0,27	<b>0,56</b>	-0,27	0,42	1,00					
Pb	<b>0,54</b>	<b>0,56</b>	0,09	<b>-0,55</b>	-0,10	0,16	-0,36	<b>-0,59</b>	1,00				
Zn	-0,31	-0,20	<b>0,73</b>	0,48	-0,05	-0,50	0,30	0,41	-0,25	1,00			
Br	0,27	-0,04	-0,23	-0,15	0,30	0,16	0,08	0,29	-0,02	-0,21	1,00		
V	0,47	0,44	-0,38	-0,55	-0,04	0,16	<b>-0,73</b>	-0,45	<b>0,52</b>	<b>0,54</b>	-0,07	1,00	
SO4	<b>-0,69</b>	-0,04	0,15	0,25	0,22	-0,26	0,29	<b>0,70</b>	<b>-0,52</b>	0,35	-0,07	-0,18	1,00
NO3	0,24	0,11	0,10	<b>-0,62</b>	-0,40	0,31	<b>-0,74</b>	-0,50	0,26	-0,27	-0,12	0,42	-0,28

The correlation after clr transformed data (table 14) also shows different correlations as compared with correlation on untransformed data. There a significant correlation between V & Pb, V & Zn, Pb & As. Zinc and copper shows a strong positive correlation in all methods (on row, and after alr & clr transformed data's). The positive significant correlation between sulphate ion and Pb that shows on untransformed data (table 8) is negative on clr transformed data.

**Table 13** Correlation between trace elements in rock samples after a transformation of the data by additive log ratio (alr) method (with  $\alpha = 0.05$  and  $r$  critical = 0.532)

	Al	As	Co	Cu	Fe	Cr	Mg	Mn	Mo	Pb	Zn	Sr	V
Al	1,00												
As	0,40	1,00											
Co	0,41	0,53	1,00										
Cu	0,51	<b>0,66</b>	0,11	1,00									
Fe	<b>0,67</b>	0,40	<b>0,87</b>	0,24	1,00								
Cr	-0,39	-0,13	<b>0,56</b>	-0,51	0,30	1,00							
Mg	0,45	0,19	<b>0,81</b>	0,02	0,82	0,45	1,00						
Mn	<b>0,75</b>	0,41	<b>0,59</b>	0,42	0,86	-0,11	<b>0,65</b>	1,00					
Mo	<b>-0,63</b>	-0,19	-0,37	0,00	-0,43	0,16	<b>-0,60</b>	-0,45	1,00				
Pb	0,18	0,37	-0,19	0,19	-0,24	-0,52	-0,10	0,04	<b>-0,54</b>	1,00			
Zn	<b>0,93</b>	0,34	0,34	<b>0,56</b>	<b>0,69</b>	-0,41	0,41	<b>0,86</b>	-0,48	0,08	1,00		
Sr	<b>0,86</b>	0,07	0,01	0,41	0,35	<b>-0,57</b>	0,18	0,46	-0,52	0,14	<b>0,77</b>	1,00	
V	<b>0,88</b>	0,52	<b>0,74</b>	0,44	<b>0,83</b>	0,03	<b>0,71</b>	<b>0,71</b>	<b>-0,60</b>	-0,01	<b>0,78</b>	<b>0,62</b>	1,00
S	0,36	-0,21	-0,06	0,30	0,14	-0,26	0,41	0,23	-0,36	-0,05	0,35	0,47	0,32

Unlike the correlation analysis on untransformed data of trace elements in rocks, correlation on alr shows a significant association between As & Cu and non-significant association between Pb & Cu and Cu & As. There also a number of trace elements associated with vanadium element as compared to correlation analysis on untransformed data.

**Table 14** Correlation between trace elements in rock samples after a transformation of the data by centered log ratio (alr) method (with  $\alpha = 0.05$  and r critical = 0.532)

	Al	As	Co	Cu	Fe	Cr	Mg	Mn	Mo	Pb	Zn	Sr	V
Al	1,00												
As	-0,40	1,00											
Co	-0,21	0,17	1,00										
Cu	-0,02	<b>0,54</b>	-0,38	1,00									
Fe	-0,12	-0,15	<b>0,79</b>	-0,47	1,00								
Cr	<b>-0,86</b>	0,16	0,49	-0,38	0,38	1,00							
Mg	-0,04	-0,35	<b>0,69</b>	-0,52	<b>0,66</b>	0,28	1,00						
Mn	0,21	-0,09	0,17	-0,03	<b>0,60</b>	-0,22	0,31	1,00					
Mo	<b>-0,80</b>	0,41	-0,25	0,25	-0,22	<b>0,58</b>	-0,50	-0,25	1,00				
Pb	-0,29	<b>0,54</b>	-0,38	0,22	<b>-0,55</b>	0,03	-0,37	-0,15	0,38	1,00			
Zn	0,77	-0,37	-0,39	0,16	0,00	<b>-0,79</b>	-0,17	<b>0,59</b>	-0,48	-0,26	1,00		
Sr	<b>0,68</b>	-0,51	<b>-0,70</b>	0,04	-0,53	<b>-0,73</b>	-0,38	-0,16	-0,36	-0,06	0,53	1,00	
V	<b>0,59</b>	-0,23	0,52	-0,24	0,26	-0,28	0,46	-0,06	<b>-0,81</b>	<b>-0,57</b>	0,18	0,05	1,00
S	<b>-0,67</b>	0,10	-0,46	0,15	-0,44	0,40	-0,24	-0,32	<b>0,75</b>	0,51	-0,45	-0,11	<b>-0,78</b>

The clr transformed data of rock sample also shows a number of different correlations between elements as compared with untransformed and alr transformed data. Like; Cu does not show any significant correlation with among listed trace elements. In this method there is a significant negative correlation between Al with Cr, Mo and S, V & Mo, Sr & Co, Sr & Cr, V& S. There is a positive significant correlation between S & Mo and Cu & As, which is related to strong positive correlation between SO<sub>4</sub> & Mo and Cu & As on clr transformed data of water sample analysis.

Despite the observation of some bivariate correlation that does not observed in untransformed data, the bivariate correlation analysis of transformed data does not improve the relation of observed pollutants which are above maximum tolerable limit (As, Pb, Zn and F). This could be because of; in compositional data analysis, data are transformed in logratio(Aitchison, 1999 ) which is a logarithmic function. This logarithmic function removes the influence of censored or anomalous values in the correlation analysis. Carranza also discovered that



Logratio transformation of stream sediment geochemical data does not improve mapping of pathfinder element anomalies which are reflecting the presence of mineralization (Carranza, 2011). Therefore; the logratio method of compositional data analysis is not improving the analysis of bivariate relation in contaminant study, because it obscure anomalous values which are the crucial values that cause different biotoxic effect to human health.

## 6. 6. Multi Variant association of trace elements using Principal component analysis

Principal component analysis (PCA) was performed in *past* statistical software used to identify the multi element association in the study area. On this analysis the element loadings on each factors which are considered to be the measure of the strength of element associations in a factor varies from +1 to -1. The table below presents the principal component (PC) loadings for possible components of different element concentration in the data. Loadings, that represent the importance of the variables for the components are bold and highlighted for positive and negative value

### 6.6.1 Multivariate analysis in water samples analysis data

**Table 15** Component Matrix for water sample analysis data and its component eigenvalue and percent of variance

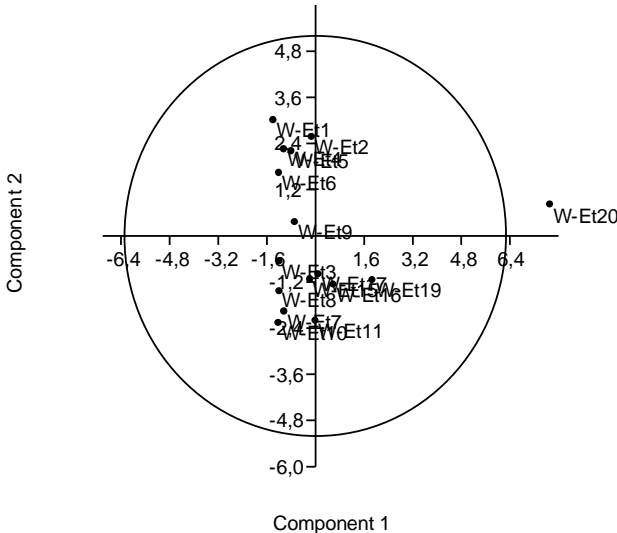
	Components						
	1	2	3	4	5	6	7
As	-0,20	<b>0,58</b>	0,44	-0,46	0,21	0,06	0,31
Co	0,08	<b>0,71</b>	-0,27	-0,02	-0,58	0,07	-0,19
Cu	<b>0,87</b>	0,36	-0,25	-0,18	0,01	-0,04	0,04
Fe	<b>0,83</b>	-0,11	-0,14	-0,16	0,12	0,45	0,01
F	0,26	0,47	<b>0,64</b>	-0,29	0,14	-0,10	-0,24
Mg	0,01	<b>0,84</b>	0,07	0,32	-0,12	-0,15	0,18
Mn	<b>0,51</b>	-0,31	0,45	0,30	-0,31	0,27	0,36
Mo	<b>0,78</b>	-0,15	0,37	0,20	0,05	-0,22	-0,23
Pb	<b>0,92</b>	0,15	-0,26	-0,19	0,11	-0,02	0,09
Zn	<b>0,91</b>	0,21	-0,30	-0,16	0,07	-0,03	-0,02
Br	0,32	<b>0,55</b>	0,31	<b>0,54</b>	0,11	0,32	-0,22
V	-0,34	<b>0,84</b>	-0,03	-0,18	-0,09	-0,02	0,09
SO4	<b>0,79</b>	-0,19	0,12	0,18	-0,13	-0,43	0,18
NO3	-0,17	0,48	-0,37	0,56	0,43	-0,06	0,13

PC	Eigenvalue	% variance
1	4,95	35,39
2	3,37	24,10
3	1,50	10,75
4	1,32	9,46
5	0,76	5,48
6	0,66	4,75
7	0,52	3,73

On the principal component analysis of elements in water samples on component matrix (table 17), the first three components explain 35.39 %, 24.1% and 10.75% of the variance and eigenvalues greater than one. The other components are not as important, they explain low variance and their eigenvalues are less than one and only can indicating that these components are related to more local effects than the first three components.

Component one shows positive loadings for most of elements. It shows positive and strong loadings that indicates the association of Cu, Fe, Mo, Mn, Pb, Zn & SO<sub>4</sub>. Component two is characterized by strong positive loading of As, Co, Mg, Br, & V. Component three and four only shows single strong positive loadings of F & Br respectively.



**Figure 16** Scatter plot of component one and component two of water sample principal component analysis

The scatter plot of component one and two (fig 16) demonstrates three clusters and the sample at station W-Et20 forms a single cluster out of the 95 % variability of the clusters which means it varies much differently than other water samples in the data, .

The multi element association of Cu, Fe, Mo and Mn with Pb and Zn could indicate that despite their recordings below maximum tolerable limit, they could contribute as additive and synergetic effect in the cause of this liver disease. The association of SO<sub>4</sub> ion also indicates the source rock might be related with sulphide minerals. Sample number W-Et20 in scatter plot of component one and two also indicates that how anomalous is such sample station as compared to other sample stations. This also supports the association of water source in this station with the liver disease incidence in eastern part of the study area.

The strong positive association of As with Co, Mg, Br, & V at component two also indicates that there could be a contribution of such elements as additive and synergetic effect in the

cause of liver disease at the western part of the study area (fig 14) at which arsenic is above maximum tolerable limit of WHO guideline value.

The single loading of fluorine and bromide might also indicate that these elements are varies alone rather than in association with other pollutants and their synergetic and additive effect with other geochemical elements could be less than lead and zinc elements.

### 6.6.2 Multivariate analysis in rock samples analysis

**Table 16** Component Matrix for rock sample analysis data and its components eigenvalue and percent of variance in each component

	Components						
	1	2	3	4	5	6	7
Al	<b>0,89</b>	0,27	-0,15	-0,21	-0,23	0,01	0,12
As	0,36	-0,24	<b>0,84</b>	0,00	-0,12	0,26	-0,13
Co	-0,22	<b>0,91</b>	0,31	-0,06	0,06	0,10	0,01
Cu	<b>0,52</b>	-0,34	<b>0,70</b>	-0,03	0,11	0,31	0,11
Fe	0,35	<b>0,90</b>	0,08	0,19	-0,12	0,00	-0,05
Cr	<b>-0,62</b>	<b>0,72</b>	0,13	-0,02	-0,02	0,11	0,14
Mg	-0,43	<b>0,82</b>	0,24	-0,03	0,27	0,06	0,06
Mn	0,34	0,16	0,12	<b>0,88</b>	0,21	-0,06	0,15
Mo	-0,49	-0,52	-0,25	0,28	-0,45	0,31	0,22
Pb	0,20	-0,38	<b>0,74</b>	-0,22	0,16	-0,39	0,17
Zn	<b>0,71</b>	0,00	-0,19	<b>0,65</b>	0,13	0,01	-0,11
Sr	<b>0,79</b>	0,23	-0,44	-0,25	0,02	-0,04	0,20
V	<b>0,75</b>	0,46	-0,04	-0,26	-0,35	0,07	-0,06
S	0,26	-0,21	-0,44	-0,29	<b>0,71</b>	0,31	0,01

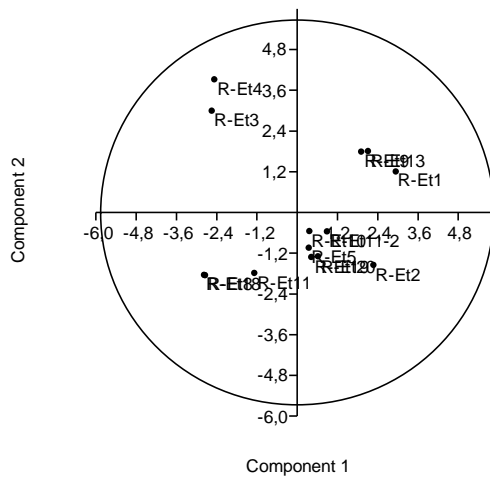
  

PC	Eigenvalue	% variance
1	4,07	29,10
2	3,82	27,31
3	2,43	17,33
4	1,62	11,58
5	1,10	7,83
6	0,56	3,96
7	0,23	1,62

The Principal component matrix of rock samples (table18) shows that the first five components explain 29.10 %, 27.31%, 17.33%, 11.58% and 7.83% of the variance and eigenvalues greater than one. The other components explain low variance and their eigenvalues are less than one.

Component one shows positive and strong positive loadings of different elements that show the association of Al, Cu, Sr, Zn & V and a strong negative loading of Cr. Component two is characterized by strong positive loading of Co, Fe, Cr & Mg. Component three also shows strong positive loadings of As, Cu, & Pb , component four between Mn & Zn and a single loading of S on component five. Like the bivariate correlation analysis this multivariate analysis of trace elements on rock also gives different association between geochemical elements

as compared to the multivariate association in water. There is no observed association of elements of those at which their concentration is above MTI in water samples.



**Figure 17** Scatter plot of component one and component two of rock sample principal component analysis

The scatter plot of component one and two (fig 17) also shows a number of clusters but all samples are within the 95 % variability of clusters. This indicates that the distributions of multi elements in different rock samples are comparable as compared to in water samples.

### 6.6.3 Multivariate analysis in soil samples analysis

**Table 17** Component Matrix for soil sample analysis data and its components eigenvalue and percent of variance in each component

	Components						
	1	2	3	4	5	6	7
Al	0,58	-0,42	0,38	-0,48	-0,10	0,10	0,30
As	0,00	<b>-0,62</b>	0,50	0,53	-0,01	0,16	-0,24
Co	<b>0,85</b>	-0,05	-0,22	0,38	-0,07	0,02	0,18
Cu	0,14	-0,05	<b>0,82</b>	0,27	0,07	-0,47	0,09
Fe	<b>0,86</b>	0,06	0,05	0,42	0,21	0,17	0,04
Cr	<b>0,64</b>	0,42	-0,51	-0,11	0,07	-0,28	-0,24
Mg	<b>0,89</b>	0,36	0,25	-0,07	-0,06	0,02	-0,01
Mn	0,47	-0,09	<b>-0,77</b>	0,28	0,17	-0,08	0,17
Pb	-0,50	0,51	0,23	0,05	0,64	0,03	0,15
Zn	0,38	<b>0,81</b>	0,30	-0,02	0,02	0,33	-0,07
Sr	<b>-0,75</b>	-0,44	-0,34	0,06	0,33	0,12	0,04
V	<b>0,70</b>	<b>-0,65</b>	-0,16	-0,19	0,11	0,05	-0,07
S	-0,61	0,35	-0,22	0,37	-0,54	0,04	0,17

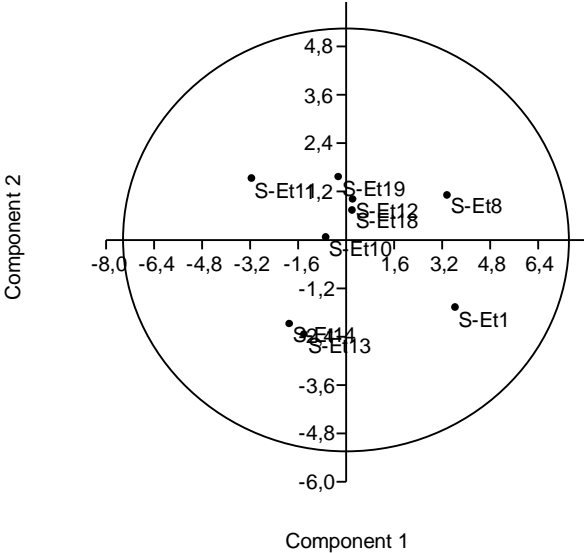
  

PC	Eigenvalue	% variance
1	5,07	39,03
2	2,53	19,43
3	2,37	18,20
4	1,18	9,08
5	0,92	7,04
6	0,50	3,83
7	0,33	2,56

The Principal component matrix of soil samples (table19) shows that the first four components explain 39.03%, 19.43%, 18.20%, and 9.08% of the variance and eigenvalues greater than one. The other components explain low variance and their eigenvalues are less than one.

There is a positive and strong loading that show the association of Co, Fe, Mg, & V and a strong negative loading of Sr at component one . Component two is characterized by strong positive loading of Zn and negative loadings of As & V. Component three also shows strong positive loadings of Cu and negative loadings of V. there is no significant loadings of elements at component four.

Like the bivariate associations, the multivariate association of elements in soil also shows different from that observed in water and rock analysis.

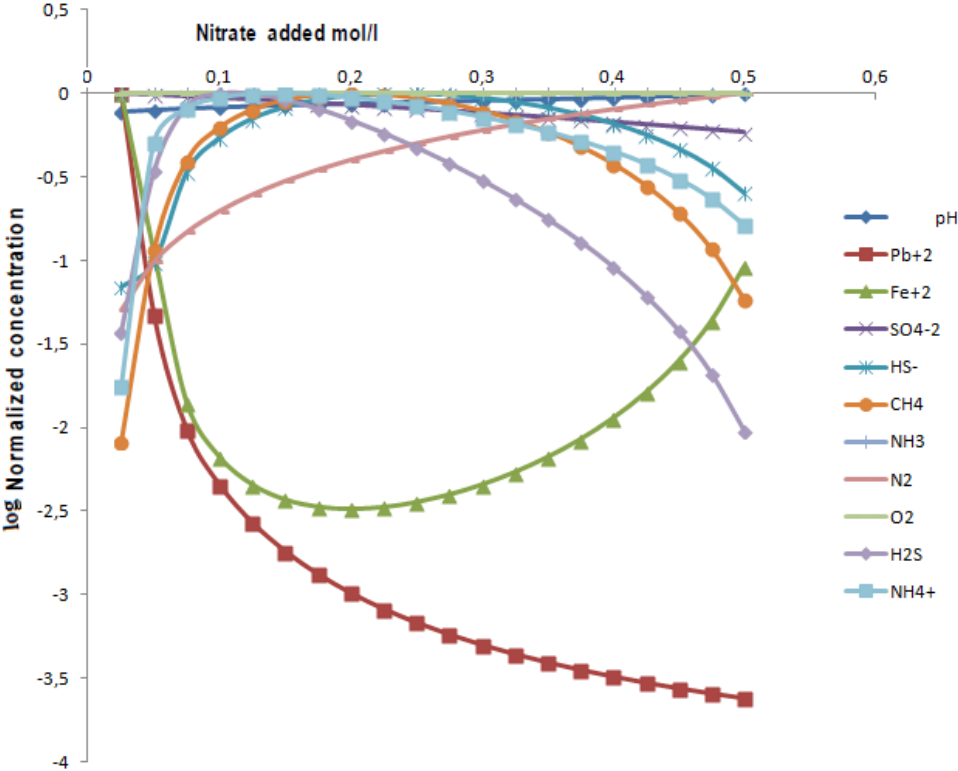


**Figure 18** Scatter plot of component one and component two of soil sample principal component analysis

The scatter plot of component one and two (fig 18) of multi variant trace elements in soil also shows a number of clusters but all samples are within the 95 % variability of the clusters. This also indicates that the distributions of multi elements in soil samples are comparable as compared to between water samples.

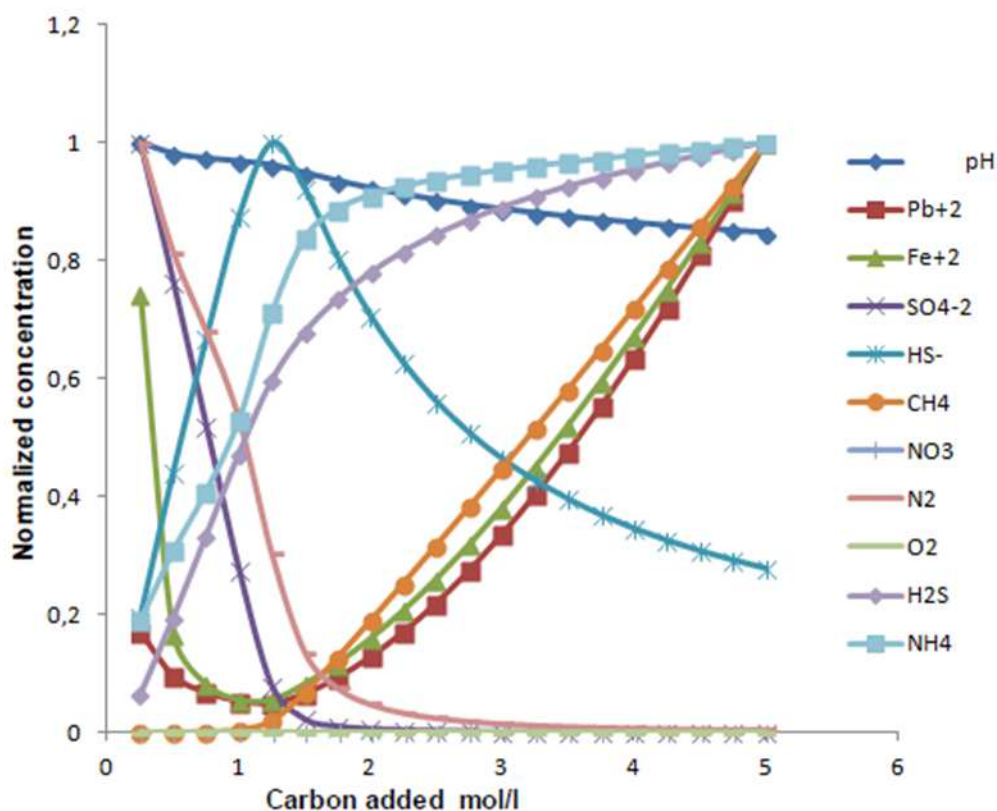
### 6.7 Simulation of Redox reaction of nitrate and dissolution of trace elements in the ground water

The simulation performs the redox reaction of nitrate and carbon with sulfide minerals in water solution. The assumption is that there is a recent anthropogenic fertilizer practice in the area. The common fertilizers are inorganic fertilizers that contain nitrate and the traditional organic fertilizer from animal waste that mostly contains carbon compounds. The carbon compounds could also be washed from the oxidized and weathered outcrop graphite rocks. So it is assumed that these nitrate and carbon from the fertilizers practice and the rock itself would percolate to the groundwater aquifer system and change the redox system of a given aquifer. The simulation performs on a water solution of sample no. W-Et 20 (at which most of the trace elements which are above maximum tolerable limit exist and its proximity to the liver incidence area) for three different cases of incremental reaction; the first one is a reaction with only nitrate is added (fig 19), the second case is with only organic carbons added (fig 20) and the third case is a reaction with both nitrate and organic carbon added (fig 20) on the aquifer system. The simulation also considers the excess of iron ion would perform precipitation as FeS.



**Figure 19** An incremental redox reaction of sulfide minerals (pyrite and galena) modeled by PHREEQC using stepwise addition of nitrate

The above plot shows that in the incremental reaction of pyrite and galena with nitrate, at the beginning there is rapid increase and decrease of concentration of different ions. There is a general trend of increasing pH of the system in this incremental reaction, which mean the solution is become more acidic. Despite the rapid increase at the beginning it shows a high rate of decrease in concentration of HS<sup>-</sup>, H<sub>2</sub>S and CH<sub>4</sub> which could indicate the change of the redox condition from reduced to oxidized solution in an oxic zone by addition of nitrate. This also supported by an increase in concentration of Fe<sup>+2</sup> from oxidation of sulfide mineral pyrite. But Pb<sup>+2</sup> ions only show a decrease in concentration. From such simulation we can deduce that nitrate could have a great contribution in dissolution of trace metals in the sulfide mineral contain aquifers. Nitrate reduction utilizing pyrite as an electron donor The transfer of electrons during the transformation of nitrate to harmless dinitrogen (N<sub>2</sub>) gas (Pyenson, 2002, Gilboa-Garber, 1971).

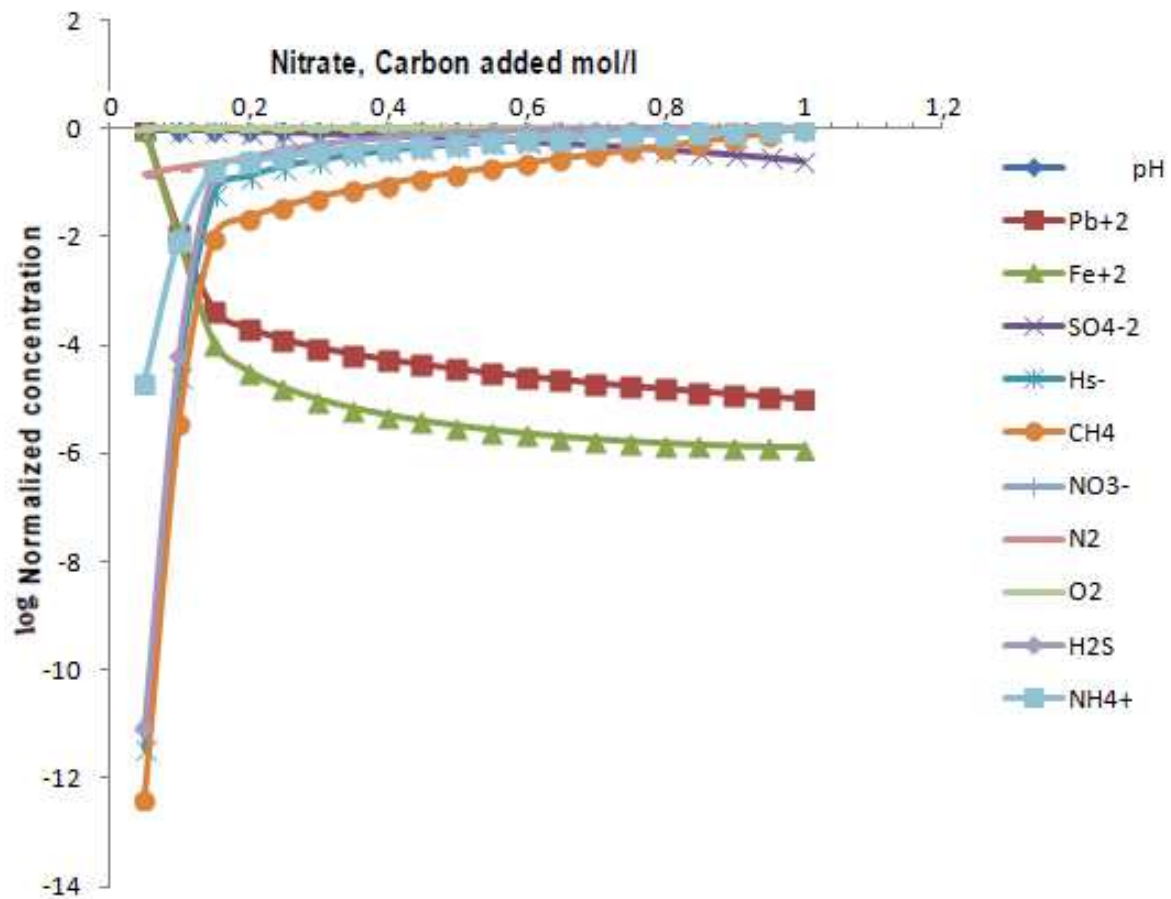


**Figure 19** An incremental redox reaction of sulfide minerals modeled by PHREEQC using stepwise addition of only carbon

An incremental reaction of pyrite and galena with carbon (fig 19) in water solution shows that there is a rapid decrease in pH of the system which indicates that the solution is become more



acidic with addition of carbon into the solution. Despite the rapid decrease at the beginning,  $\text{Pb}^{+2}$ ,  $\text{Fe}^{+2}$  and  $\text{CH}_4$  ions show a rapid rate of increase in the incremental reaction.  $\text{SO}_4^{-2}$  and  $\text{N}_2$  rapidly decreases,  $\text{HS}^-$  also shows decrease after an increase at the beginning.  $\text{H}_2\text{S}$  and  $\text{NH}_4$  also show increase in concentration in this incremental reaction. The increase in  $\text{CH}_4$  and  $\text{H}_2\text{S}$  indicates the system become much reduced and the increase in  $\text{Pb}^{+2}$ ,  $\text{Fe}^{+2}$  indicates there could be an increase in dissolution rate within reduced environment by addition of carbon.



..  
**Figure 20** An incremental redox reaction of sulfide minerals modeled by PHREEQC using stepwise addition of nitrate and carbon.

The stepwise addition of both nitrate and carbon in a water solution of incremental reaction (fig 20) shows a trend of a decrease in concentration of cations ( $\text{Fe}^{+2}$  and  $\text{Pb}^{+2}$ ) and an increase in concentration of anions. It shows that the system is become much more reduced with a rapid increase of methane,  $\text{HS}^-$  and  $\text{H}_2\text{S}$ . The reaction of nitrate and methane results an increase in methane and ammonia by reduction of nitrate. This shows that carbon reduces nitrate in the aquifer system which decreases the dissolution rate of cations.

## 6 Conclusions

The potable quality of water in the study area is poor at which most of TDS recording shows above acceptable limit. Based on WHO guideline value and its spatial association with the liver incidence area the probable cause of this liver disease could be Pb and Zn at the eastern and As at the western part of the study area. The bivariate and multivariate associations of these elements with other elements also indicate that the incidence of liver disease might be caused by the interaction of elements which is the additive or synergetic effects.

The high value of; TDS, pH, sulfate, the multi element association of Cu, Fe, Mo and Mn with Pb and Zn in water samples and high sulfur and Polar organic compounds in the rock samples indicates that the incidence of liver disease at eastern part of the study area is related to graphite muscovite schist type of rock which could be organic sulfide minerals.

Lack of pattern in association of trace elements within water, soil and rock samples could be because of the dispersion process; selective weathering of minerals and selective dissolution of elements and also the high mobility of elements due to high transmissivity of highly fractured aquifers found in the study area.

Compositional data analysis does not improve the relationship analysis between geochemical pollutants. This could be because of in compositional data analysis data are transformed in logratio which is a logarithmic function. This logarithmic and ratio function removes the influence of anomalous values which are the crucial values that cause different biotoxic effect to human health.

The reason for the recent occurrence of this liver disease could be related to the recent fertilizer practice. Nitrate from inorganic fertilizers and carbon from organic fertilizers could change the dissolution of trace elements from sulfide minerals in the anoxic zone groundwater aquifer system by change the redox system of a given aquifer.

## **7 Recommendations**

The responsible elements that cause liver disease from the investigation in the study area are probable or speculate. In order to have a full understanding of the responsible geochemical element, a chemical analysis of liver sample from the infected people is recommended.

Besides to the drinking water, humans could expose to trace element pollutants by other mode of exposures like bioconcentration by plants and animals and incorporation into food cycles. Therefore the study area needs much more detail investigation that includes the different possible mode of exposure

The toxicity of a given element depends on type of speciation of an element and its chemical structure in the diet. Therefore detail study of the speciation of geochemical pollutants in water and its health effect is recommended

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