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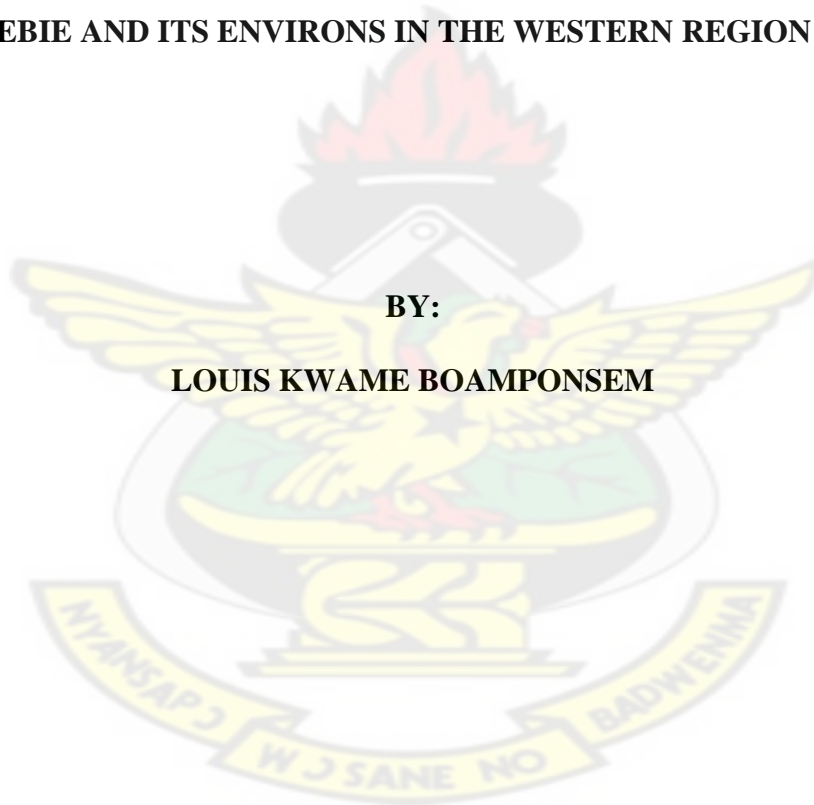
FACULTY OF BIOSCIENCE

DEPARTMENT OF ENVIRONMENTAL SCIENCE

**HEAVY METALS LEVELS IN LICHENS, SOILS, SEDIMENTS AND WATER BODIES
OF TEBEREBIE AND ITS ENVIRONS IN THE WESTERN REGION OF GHANA**

BY:

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SEPTEMBER, 2009

HEAVY METALS LEVELS IN LICHENS, SOILS, SEDIMENTS AND WATER BODIES OF
TEBEREBIE AND ITS ENVIRONS IN THE WESTERN REGION OF GHANA

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DECLARATION

It is hereby declared that this thesis is the outcome of research work undertaken by the author, any assistance obtained has been duly acknowledged. It is neither in part nor whole been presented for another degree elsewhere.

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DEDICATION

This research is dedicated to God Almighty, my father Nana Oboaman Bofotia Boa-Amponsem II (Krontihene of Sunyani Traditional Council), my mother Mrs. Theresa Naana Boa-Amponsem, and my sister Mavis Adwoa Darkowah Boa-Amponsem (University for Development Studies, Wa Campus).

KNUST



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ABSTRACT

Mining and industrial processing are among the main sources of heavy metals contamination in the environment. Heavy metals may accumulate to toxic level which can cause a potential risk to human health. Several years of large scale and small scale mining in Teberebie and surrounding areas are a potential source of environmental pollution. Consequently, *in situ* lichens (*Parmelia sulcata*), soils, water and sediments samples have been used in assessing atmospheric, soil and stream heavy metal contamination in Teberebie, Mile 6, Mile 7 and Mile 8. The research involved the determination of total heavy metals (As, Al, Cd, Co, Cu, Hg, Mn, Sb, Th, and V) levels in the environmental samples using instrumental neutron activation analysis (INAA). The atmospheric pollution levels were evaluated using pollution index factor (PIF) and pollution load index (PLI). The results from the lichen revealed high levels of Sb, Mn, Cu, V, Al, Co, Hg, Cd and As in excess of the background values. The enrichment factor (EF) and estimated background concentration (EC) analyses of the lichen data using Al as a reference element showed that Sb, Mn, V, Co, Hg, Cd and Th were enriched in the lichens by active biological processes from atmospheric deposition, clearly indicating point and non-point origins of these elements. Pollution source identification of heavy metals in lichens using principal component analysis (PCA) and cluster analysis (CA) resulted in 3 groups of elements. Group 1 (Sb, V, Al and Cu) may have resulted from both anthropogenic activities (gold mining and agricultural activities) and natural sources, Group 2 (Mn, Hg, Co and As) from anthropogenic (gold mining) activities, whereas the source of Group 3 (Cd and Th) could be natural. Also, the sampling sites were clustered into 2 groups as relatively moderate pollution (MP) sites and a relatively high polluted (HP) sites. The PCA, CA and PLI results suggest that atmospheric deposition of point source pollutants decrease with distance from the pollution sources. The levels of As, Cd, Co,

Cu, Th and Hg in soil samples from all sampling points were lower than reference values reported in literature and within the normal soil range values. This indicates that the mining activities have not affected the soils in the study area greatly. The results generally showed elevated levels of all the ten examined elements in water and sediment samples. Angonabeng and Bediabewu rivers recorded high levels (exceeding WHO guidelines for drinking water) for Sb, Mn, Cu, Al, Co, Hg and As in their water samples. The Contamination Factor (CF) assessment of the contamination of sediments has revealed that Teberebie springs are mainly polluted with Sb, Mn, V, Al and Cd, and unpolluted to slightly polluted with Cu, Co, As, Hg and Th. Mile 7 spring sediment is mainly polluted with Sb, and slightly to unpolluted with Mn, V, Cu, Co, Al, Hg, As, Cd and Th. The water-sediment correlation matrix, Pollution Load Index (PLI) and the Contamination degree (C_d) results from this study have revealed that the amount of the examined elements in the water depends on the amount in the sediments, and they are directly proportional. The water quality with respect to the monitored elements in borehole water in general can be said to be good. However, there were high levels of Mn and Al in the borehole water samples which exceeded the WHO guidelines for drinking water quality.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Ghana is an important gold-producing country with mining operations since the late 19th century (Akabzaa and Darimani, 2001; Kumi-Boateng, 2007). Ghana produces about one third of the world's yearly gold production (Griffis *et al.*, 2002; Kumi-Boateng, 2007). About 40 % of gross foreign exchange earnings of the country come from the mining sector. It has been reported by Aryee (2001) that the mining sector in Ghana generates about 5.7% of gross domestic product (GDP). The industry also has linkages to other sectors and is a major employer in the areas where they operate. Mining companies have also contributed to the development of the areas by the provision of social amenities and infrastructure such as schools, hospitals and roads (Addy, 1998; Asklund and Eldvall, 2005).

In recent times, a lot of attention has been drawn to the mining industry and its adverse impacts on the environment. In spite of the socio-economic benefits of gold mining to the local communities and the country as a whole, a considerable stress has been put on the environment and basic life support systems, thus posing potential threat to the health of the people (Nyarko *et al.*, 2004). In Ghana, some studies have been conducted on heavy metal pollution in some mining towns or areas (Kortatsi, 2004; Nyarko *et al.*, 2004; Serfor-Armah *et al.*, 2006; Akabzaa *et al.*, 2007). Most of these studies have indicated that heavy metals are high in environmental samples collected from these mining areas. Serfor-Armah *et al.* (2006) reported high levels of arsenic and antimony in some streams of Prestea, a gold mining town in the western part of

Ghana. According to a research conducted by Kumi-Boateng (2007), soil and sediment samples from Obuasi (a major gold mining town in Ghana) contained high arsenic concentrations. Nyarko *et al.* (2004) reported high levels of some heavy metals in the atmosphere of Obuasi and its surrounding villages.

The unfortunate situation has arisen because of the nature of the ore and the method of processing gold at the mines. The ore exists as finely dispersed quartz vein lodes, either in the free form or contacted within mineralized rocks in association with iron pyrites (FeS_2) and arsenopyrites (FeAsS) (Nyarko *et al.*, 2004). Other heavy metals associated with the gold, such as arsenic (As), cadmium (Cd), lead (Pb), zinc (Zn) and copper (Cu) may be released through processing to enter streams. These heavy metals may lead to environmental pollution (Teng *et al.*, 2004; Kumi-Boateng, 2007). Mine waste and tailings may disperse into the atmosphere, soils and streams. Mercury (Hg) may also enter streams if miners use it to recover fine particles of gold. Gold ores may contain significant amounts of mercury, and processing of the ores to recover gold may generate mercury air emissions (US EPA, 2001). Most gold ore processing relies on cyanide leaching to extract gold from the ore. The gold-bearing cyanide solution is then concentrated, and the gold is recovered and further purified (US EPA, 2001). Occasionally, cyanide and its associated heavy metals are released accidentally or deliberately into the environment posing short and long term effects to living organisms. For instance, villages in the Wassa West District of the Western Region of Ghana were hit by the spillage of thousands of cubic metres of mine wastewater contaminated with cyanide and heavy metals. The cyanide-laced waste contaminated the Asuman river on October 16, 2001 when a tailings dam belonging to the Goldfields Ltd ruptured during a mine operation. Many dead fishes, crabs and birds were

seen littering the banks of the river; others floated on the surface of the river which is the only source of drinking water for Abekoase, Huni and surrounding villages. Scientists were apprehensive that the cyanide and heavy metal residue from the spill could remain for decades thereby posing health and environmental threat to the people and wildlife in the area (Anane, 2001).

Heavy metals are among the most dangerous groups of anthropogenic environmental pollutants due to their potential toxicity and persistence in the environment (Carreras *et al.*, 2009). Heavy metals can cause health problems at higher exposures and destroy aquatic organisms when leached into water bodies. Heavy metals contamination of aquatic environments has raised serious concern due to their tendency to accumulate in aquatic habitats. Heavy metals residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which in turn may enter the human food chain and result in health problems (Sin *et al.*, 2001). Over the last decades, there has been a growing concern about atmospheric particulates (including heavy metals) because evidence has shown that they are associated with respiratory and cardiovascular diseases (Dockery *et al.*, 1993; Nyarko *et al.*, 2004; Godinho *et al.*, 2008), severe intestinal upsets, keratosis and skin cancer (Steinnes and Krog, 1997) in humans.

Several environmental indicators have been used in environmental monitoring and assessment studies. Among the widely used pollution monitors are soil, sediment, water and biomonitors (such as lichen and moss). Lichens have been used worldwide as air pollution monitors (Loppi *et al.*, 1999; Tamara *et al.*, 2003). Lichens are used as pollution monitors because they concentrate a variety of pollutants in their tissues (Aznar *et al.*, 2008). For example, in Ghana, Nyarko *et al.*

(2004) used *in situ* lichen samples as biomonitors to reveal that the atmosphere of Obuasi and its environs are highly polluted with arsenic and vanadium. Lichens and bryophytes not only contribute to biodiversity but also play integral roles in nutrient and hydrological cycles, and are valuable sources of forage, shelter, and nesting material for mammals, birds and invertebrates (McCune and Geiser, 1995; Brodo *et al.*, 2001). Generally, loss of biological diversity or population within or across groups of organisms contributes to a decline in ecosystem stability, functionality and productivity (Eldredge, 1998; Novacek, 2001). The geochemical investigation of sediments is of major importance in the study of aquatic systems, as they provide information about the heavy metals dissolved (Das, 2005). The sediment of any water body contains a historical record of the natural and anthropogenic fluxes of heavy metals received into the water basin (Kemp and Thomas, 1976). Studies by Das (2005), Aksoy *et al.* (2005) and Nguyen *et al.* (2005) proved that sediment samples can be used to study heavy metals (including mercury, vanadium and arsenic) levels in water bodies. Using sediment and water samples, Serfor-Armah *et al.* (2006) showed that some streams in Prestea are polluted with arsenic and antimony. A study by Akabzaa *et al.* (2007) showed that water resources especially surface water of Obuasi mine vicinity have significant amount of mercury, arsenic and other heavy metals. The need to assess the quality of some water bodies and their sediments in terms of their metallic load in all the mining areas of Ghana becomes imperative since water from these sources is being used for domestic irrigation and livestock activities by people living in the catchment areas, in view of the health implications that cut across the food strata.

This study assesses the levels of some heavy metals (aluminium, antimony, arsenic, cadmium, cobalt, copper, manganese, mercury, thorium and vanadium) in lichens (*Parmelia sulcata.*),

soils, water and sediments samples from the gold mining community of Teberebie and its environs (i.e., Mile 6, Mile 7 and Mile 8) over a 12-month period, using neutron activation analysis supported by multivariate statistical methods. It will provide a valuable tool in developing assessment strategies for effective air, soil and water monitoring studies in areas exposed to gold mining activities.

1.2 PROBLEM STATEMENT

In Ghana, information about atmospheric pollutant levels in industrial and mining areas is scanty. Most available data have involved the use of air samplers for Total Suspended Particulates (TSP) or Particulate Matter (PM)-10. As noted by Affum *et al.* (2008), direct air sampling methods are not only expensive but also require trained manpower which may not be available. In view of this, there is the need to adopt other effective approaches to the conventional or direct air sampling methods, of which lichens are among the best alternatives. The use of lichens as bioindicators of atmospheric pollution has also not received much attention in Ghana. Few works in this area of study include that of Affum *et al.* (2008), where lichen transplants were successfully used to assess the pollution status along a major road in Accra due to vehicular traffic. Nyarko *et al.* (2005) and Nyarko *et al.* (2004, 2008) used *in situ* lichens to monitor atmospheric heavy metal deposition due to gold mining activities in the Prestea and Obuasi and their environs, respectively.

Most studies on heavy metal pollution have concentrated on other mining areas such as Obuasi and Prestea (e.g., Nyarko *et al.*, 2004; Serfor-Armah *et al.*, 2006; Akabzaa *et al.*, 2007). Only limited literature is available on heavy metal pollution in the Tarkwa gold-mining district

(Kortatsi, 2004; Essumang *et al.*, 2007). No literature exists on the use of lichens in monitoring atmospheric trace element deposition in the Tarkwa area. Several years of large scale mining companies [Ghana Australian Goldfields (GAG), Teberebie Goldfields Limited (TGL), Iduapriem Anlogold Ashanti Mines (IAAM)] and small scale mining (including illegal *galamsey* operators) activities in the Tarkwa and surrounding areas are a potential source of environmental pollution. Although the Environmental Protection Agency (EPA) of Ghana plays a supervisory and regulatory role over the activities of the mining companies, the communities are faced with environmental pollution. The unfortunate incident of cyanide-rich water spillage in the Angonabeng and Asuman streams as a result of partial failure of TGL in June 1997 and Goldfields Ghana Limited in October 2001 also aggravated the environmental concerns already intimated by the people (Anane, 2001). There is no pipe-borne water in these communities and so the inhabitants rely on boreholes and some streams in the locality.

1.3 OBJECTIVES OF THE STUDY

The main objective of this study is to determine heavy metals pollution of the gold mining town of Teberebie and its environs in the Western Region of Ghana, by assessing heavy metals concentrations in lichens, soil, water and sediment samples. The specific objectives of this research were:

1. to quantify air pollution by monitored elements in the study area using Pollution Load Index (PLI)
2. to quantify soil, and stream sediment pollution by monitored elements in study area using PLI, Geoaccumulation Index (Igeo), and Enrichment factor (EF).

3. to quantify stream pollution by monitored elements in the study area using Contamination degree (Cd).
4. to assess the level of the monitored elements in borehole water of Teberebie and Mile 7
5. to evaluate the spatial similarities or differences between sampling sites using Principal Component Analysis (PCA) and Cluster Analysis (CA).



CHAPTER TWO

LITERATURE REVIEW

2.1 HEAVY METALS

Heavy metals have been defined differently by many sectors of academia. Many different definitions have been proposed – some based on density, some on atomic weight, and some on chemical properties or toxicity (Duffus, 2002). Heavy metals are natural components of the earth crust which cannot be degraded or destroyed [EPA (SA), 2009]. Living organisms require varying amounts of some heavy metals. For example, iron, cobalt, copper, manganese, selenium, molybdenum and zinc are essential to human body (Duffus, 2002). Excessive levels, however, can be damaging to many organisms. Some heavy metals such as mercury, plutonium and lead are toxic metals that have no known vital or beneficial effect on organisms, and their accumulation over time in the bodies of animals can cause serious health problems (Lane and Morel, 2000).

Heavy metal pollution can arise from many sources. These sources may include industrial point sources, such as present and former mining activities, foundries, pesticides and smelters (including smelting of copper and the preparation of nuclear fuels). Other sources include combustion by-products, and vehicular traffic. It was reported that heavy metal pollution is not only a problem associated with areas of intensive industry but roadways and automobiles are now considered to be one of the largest sources of heavy metals (Conservation Current, 2005). Zinc (from tire wear, motor oil, grease, brake emissions and corrosion of galvanized parts), copper and lead (from leaded gasoline, tire wear, lubricating oil and grease and bearing wear)

are three of the commonest heavy metals released from road travel, accounting for at least 90 of the total metals in road runoff (Conservation Current, 2005).

Some common metals from road runoff are iron (from auto body rust and engine parts), copper (from bearing wear, engine parts and brake emissions), cadmium (from tire wear, fuel burning and batteries), chromium (from air conditioning coolants, engine parts and brake emissions), nickel (from diesel fuel, gasoline, lubricating oil, brake emissions) and aluminium (from auto body corrosion).

2.2 MINING AND HEAVY METALS

The mining industry is a major source of heavy metal pollutants in the environment. Various heavy metals such as manganese, arsenic, cadmium, mercury and vanadium are emitted from the mines (EDIE, 2001). The release into the environment of hazardous contaminated materials, from and around the operational areas of the mining plant sites [such as cyanide in leach (CIL) mill, process tanks, reagent storage tanks and pipelines] have been found to be the main source of the metals. The release of toxic materials into the environment, as a result of rainfall runoff from and around the operational area of the mine plants, has the potential to cause soil and water pollution.

Spillage in an event of pipeline failure or leakage from mines is a potential source of heavy metal pollution. Spillage of chemicals (including heavy metals), hydrocarbons and other substances could contaminate the soil and water sources. Inappropriate disposal of waste generated by CIL facility (e.g. oil, containers) may lead to heavy metal pollution. There is also the potential for

cyanide and its associated heavy metals pollution either by direct escape of cyanide from the CIL circuit or by seepage or spillage in the plant area (Beischer, 2006). Some mining communities in Ghana have experienced sporadic cyanide contaminations. For instance, the Kyekyewere community within the concession of Abosso Goldfields Limited (AGL) complained of occasional cyanide leakage from pipes close to the community (Akabzaa and Darimani, 2001).

Mine tailings are potential heavy metals source. The separation processes used for most metals do not extract all the minerals present. The tailings that accumulate in the environment may contain quantities of toxic metals and other minerals, as well as residues of the chemicals used for extraction. The finely ground minerals from processing makes contaminants such as arsenic, cadmium, antimony, copper, lead and zinc, bound up in solid rock accessible to water (Beischer, 2006). The tailings may be released directly to rivers and other water bodies and this may introduce large amounts of suspended solids and contaminants directly into aquatic habitats. Many mining operations especially those extracting ores that contain sulphides such as Ni, Cu, Fe, Zn, Cd and Pb may produce acidic and metal-bearing solutions (Serfor-Armah *et al.*, 2006). The combination of acids and metal-bearing solutions can have severe effects on the ecology of local watercourse as a result of the metals trapped in sediments (Serfor-Armah *et al.*, 2006).

Dust blowing from mine waste dumps may carry pollutants including heavy metals into the atmosphere causing air, water and land pollution (Guoli, 2009). During the dry season some mine wastes crumble to fine dust which is carried in the air by winds of even moderate force. During the rainy season some soaked wastes revert to an amorphous slurry, spreading to the near

by lowlands which are, in most cases, good agricultural soils, and into water supplies (Guoli, 2009)

The activities of galamsey operators in mining communities also contribute immensely to heavy metal pollution in the streams by increasing the mercury content. Galamsey operators combine significant volumes of water from the streams with mercury for gold processing (Akabzaa and Darimani, 2001).

2.3 TOXICITY OF HEAVY METALS

Heightened concern for reduction in environmental pollution over the past decades has stimulated active continuing research and literature on the toxicology of heavy metals. Virtually all metals can produce toxicity when ingested in sufficient quantities, but there are several of them which are especially important because they produce toxicity at low concentrations (Hoekman, 2008).

In general, heavy metals produce their toxicity in organisms by forming complexes or “ligands” with organic compounds (Soghoian, 2008; Hoekman, 2008). These modified biological molecules lose their ability to function properly, and result in malfunction or death of the affected cells. Some heavy metals may form complexes with other materials in living organisms. These complexes may inactivate some important enzymes, systems and certain protein structures (Hoekman, 2008).

The presence of heavy metals above a certain threshold can be injurious to human health and the environment, particularly communities without alternative sources of drinking water who continue to depend on polluted streams (Akabzaa and Darimani, 2001).

2.3.1 Aluminium

Aluminium (Al) can be toxic to plants by inhibition of root growth (Delhaize and Ryan, 1995; LENNTECH, 2009). Aluminium toxicity has not been detected in grazing animals but plant growth, particularly growth of seedlings can be greatly harmed by high levels of exchangeable soil Al (Delhaize and Ryan, 1995). Excess Al may cause diseases in humans. It may hamper many metabolic processes especially turnover of calcium, phosphorus and iron (Ochmanski and Barabasz, 2000). Salts of Al may bind to DNA, RNA, inhibit enzymes such as hexokinase, acid and alkaline phosphatases, phosphodiesterase and phosphooxydase (Ochmanski and Barabasz, 2000). Aluminium salts are especially harmful to nervous, hematopoietic systems and to skeleton. Toxicity comes from substitution of Mg and Fe ions effecting disturbances in intracellular signaling, excretory functions and cellular growth (Ochmanski and Barabasz, 2000). There are observations in experimental models proving Al salts are responsible for Alzheimer disease development (Ochmanski and Barabasz, 2000; Asklund and Eldvall, 2005; LENNTECH, 2009). Aluminium has also been linked to low erythropoietin production leading to anaemia in humans (Ochmanski and Barabasz, 2000). Aluminium is also connected to nerve damage, and people with kidney damage are susceptible to Al toxicity (LENNTECH, 2009). Increased Al intake may also cause osteomalacia (vitamin D and calcium deficits) and functional lung disorder in humans (LENNTECH, 2009).

Regular Al concentrations in groundwater are about 0.4 ppm, because it is present in soils as water insoluble hydroxide (LENNTECH, 2009). It naturally occurs in waters in very low concentrations. Higher concentrations derived from mining waste may negatively affect aquatic biocoenosis. Aluminium is toxic to fish in acidic, unbuffered waters starting at a concentration of 0.1 mg/L (LENNTECH, 2009).

2.3.2 Antimony

Acute oral exposure of humans and animals to high doses of antimony (Sb) or Sb-containing compounds may cause gastrointestinal disorders (irritation, vomiting and diarrhea), respiratory difficulties, and death at extremely high doses (ATSDR, 1990). Targets for long-term exposure are the blood (hematological disorders) and liver (mild hepatotoxicity) [ATSDR, 1990]. Inhalation exposure to antimony affects the respiratory tract (pneumoconiosis, restrictive airway disorders), with secondary targets being the cardiovascular system (altered blood pressure and electrocardiograms) and histological changes of kidneys (Young, 2005a). Subchronic and chronic oral exposure may affect hematologic parameters (ATSDR, 1990). Long-term exposure to high doses of Sb has been shown to adversely affect longevity in animals (Schroeder *et al.*, 1970).

Exposure of animals to high concentrations of Sb may result in pulmonary edema and death (Price *et al.*, 1979). Long-term occupational exposure of humans has resulted in electrocardiac

disorders, respiratory disorders, and possibly increased mortality. Eye irritation due to exposure to antimony oxides has been reported for humans (Young, 2005a).

2.3.3 Arsenic

All types of arsenic exposure can cause kidney and liver damage, and in the most severe exposure there is erythrocyte hemolysis (Hoekman, 2008). It is found to cause skin and nail changes (hyperkeratosis and hyperpigmentation); sensory and motor polyneuritis; hemolytic anemia (leukopenia, proteinuria, and liver function abnormalities); inflammation of respiratory mucosa; peripheral vascular insufficiency; elevated risk of skin cancer, and cancers of lung, liver, bladder, kidney and colon (Steinnes and Krog, 1997; ESSORTMENT, 2002; Hoekman, 2008). Data obtained by the Soil Research Institute of the Council for Scientific and Industrial Research (CSIR) on As levels in top soils of some mining areas in Ghana indicated values above 300 ppm in some cases (Tetteh, 2004).

2.3.4 Cadmium

Exposure to cadmium (Cd) and its compounds may occur in both occupational and environmental settings, the latter primarily via the diet and drinking water (ATSDR, 1989). Acute oral exposure to 20-30 g of Cd has caused fatalities in humans (Young, 2005b). Exposure to lower amounts may cause gastrointestinal irritation, vomiting, abdominal pain, and diarrhea (Young, 2005b). Long term exposure to cadmium primarily affects the kidneys, resulting in tubular proteinosis (Goyer, 1991). Inhalation exposure to cadmium and its compounds may result in effects including headache, chest pains, muscular weakness, pulmonary edema, and death (USAF, 1990). The 1-minute and 10-minute lethal concentration of cadmium for humans has

been estimated to be about 2,500 and 250 mg/m³, respectively (RIAS, 2005). An 8-hour time-weighted-average (TWA) exposure level of 5 mg/m³ has been estimated for lethal effects of inhalation exposure to cadmium, and exposure to 1 mg/m³ is considered to be immediately dangerous to human health (Friberg *et al*, 1974). Renal toxicity (tubular proteinosis) may also result from inhalation exposure to cadmium (Goyer, 1991).

Inhalation of cadmium fumes or dust may result in a wide range of effects, including a metallic taste, headache, dyspnea, chest pains, cough with foamy or bloody sputum, and muscular weakness (Young, 2005b). Severe exposure may result in pulmonary edema and death (USAF, 1990).

2.3.5 Cobalt

Natural sources of cobalt (Co) in the environment are soil, dust, seawater, volcanic eruptions and forest fires. It is also released into the environment from burning coal and oil as well as from car, truck and airplane exhausts, and from industrial processes that use the metal or its compounds (OMOE, 2008).

The average concentration of cobalt in soils throughout the world is 8 ppm (OMOE, 2008). The toxic effects on plants are unlikely to occur below soil Co concentrations of 40 ppm. However, the more acidic the soil is, the greater the potential for cobalt toxicity, at any concentration (OMOE, 2008). Effects on the lungs, including asthma, pneumonia and wheezing, have been found in workers who breathed high levels of Co in the air (OMOE, 2008). Elevated concentrations may result in serious liver and kidney damage, gastrointestinal distress and, in a

lesser scale, vomiting and nausea (Virkutyte and Silanpaa, 2006). Animals exposed to high concentrations of cobalt during pregnancy have problems with the development of the foetus (OMOE, 2008).

2.3.6 Copper

Most copper (Cu) compounds found in air, soil and water are strongly attached to dust or embedded in minerals (MDH, 2006). One may be exposed to Cu by breathing air, eating food, or drinking water containing Cu as well as through skin contact with soil, water or other copper-containing substances. Copper is an essential element for living organisms, including humans, and small amounts is necessary in diets to ensure good health (Vitosh *et al.*, 1994; MDH, 2006). However, too much Cu can cause adverse health effects in humans, including vomiting, diarrhea, stomach cramps, nausea, irritation of skin, eyes and respiratory tract (Kegley *et al.*, 2009; MDH, 2006). Copper has also been associated with liver damage and kidney disease (MDH, 2006).

2.3.7 Mercury

Mercury (Hg) is a naturally occurring element existing in multiple forms and in various oxidation states. In the environment, Hg may undergo transformations among its various forms and among its oxidation states (Young, 2005c).

Organic forms of mercury compounds are particularly toxic. Mercury can combine with a methyl group to become methyl mercury. This form of Hg is found in a variety of environmental pollution situations and can produce a range of toxicities (Hoekman, 2008). Organic mercury, especially methyl mercury, rapidly enters the central nervous system resulting in behavioral and

neuromotor disorders (ATSDR, 1989b; Goyer, 1991). Exposure to organic mercury causes central nervous system effects, especially in the fetus and neonate (Marsh *et al.*, 1987). Although any exposure to organic mercury compounds will contribute to the body burden of mercury, exposure during pregnancy or the postnatal period has the most significant consequences (Young, 2005c).

In the gastrointestinal tract, acute poisoning by mercury produces a sloughing away of the mucosa to an extent where pieces of the intestinal mucosa can be found in the stools. Mercury also breaks down barriers in the capillaries resulting in edema throughout the body. A range of neurological toxicities are also common. These include lethargy and tremor (Hoekman, 2008). Inhalation of mercury vapour may cause irritation of the respiratory tract, renal disorders, renal toxicity and death (ATSDR, 1989b).

2.3.8 Manganese

Manganese (Mn) is an essential element that is found in living systems most often in the +2 valence (Keen *et al.*, 1988; Stokinger, 1981). It is an essential trace element in humans that can bring forth a variety of serious toxic responses upon prolonged exposure to elevated concentrations either orally or by inhalation. Normal nutritional requirements of Mn are satisfied through the diet, which is the normal source of the element, with minor contributions from water and air (US EPA, 1984). Toxic exposures occur largely due to particulate material in the air from mining and manufacturing activities (Francis and Forsyth, 2005). This heavy metal is frequently associated with iron deposits (Hoekman, 2008).

2.3.9 Thorium

In the environment, thorium (Th) exists in combination with other minerals, such as silica. Small amount of Th is present in all rocks, soil, water, plants and animals. Soil contains an average of about 6 ppm of Th (ATSDR, 1991). Mining Th or making products that contain it may also release Th into the environment (ATSDR, 1991).

2.3.10 Vanadium

The average concentration of vanadium (V) in the earth's crust is about 150 µg/g; concentrations in soil vary in the range 3-310 µg/g and may reach high values (up to 400 µg/g) in areas polluted by fly ash. The concentration of V in water is largely dependent on geographical location and ranges from 0.2 to more than 100 µg/litre in freshwater, and from 0.2 to 29 µg/litre in seawater (Waters, 1977). The major anthropogenic point sources of atmospheric emission are metallurgical works, burning of crude or residual oil and coal (Anderson, 1973). Concentrations of V in drinking water may range from about 0.2 to >100 µg/litre (WHO Regional Office for Europe, 2000).

People living near hazardous wastes sites containing vanadium may experience respiratory problems and exposure to high levels of vanadium through inhalation can result in inflammation of the lungs and other parts of the respiratory tract (Nyarko *et al.*, 2004). Some epidemiological data have shown positive correlations between the vanadium content of urban air and mortality from bronchitis, pneumonia, nephritis, cancer (other than lung cancer in males) [Stocks, 1960] and "heart disease" (WHO Regional Office for Europe, 2000).

2.4 POLLUTION MONITORS

2.4.1 Biomonitors

Biomonitoring is an experimental method used to measure the response of organisms to pollution (Carreras *et al.*, 2009). Biomonitoring allows continuous observation of an area with the help of bio-indicators, an organism (or part of it) that reveals the presence of a substance in its surroundings with observable and measurable changes, which can be distinguished from the effects of natural stress (Tamara *et al.*, 2003)

Biomonitors are sensitive to pollutants, radioactive species, atmospheric particulates, heavy metals and other pollutants in the environment. Biomonitoring has several advantages over conventional air samplers such as: low cost, non-dependence on power supply, easier sampling and sample handling and easier determination of trace elements (Bargagli, 1995; Godinho *et al.*, 2008). Biomonitors which have been extensively used in the study of pollution (air, land and water) worldwide include lichen, moss, plants, animals, aquatic flora and fauna.

2.4.1.1 Lichens

Lichens are composite organisms formed by a fungus and a photosynthetic green alga and/or a blue-green bacterium that commonly grow on rocks, walls and trees. They have been effectively used as biomonitors of metal contamination in the atmosphere either by sampling of the organism *in situ* or by using the transplantation technique (Bargagli, 1995; Loppi *et al.*, 1999; Ng *et al.*, 2005; Aznar *et al.*, 2008; Policnik *et al.*, 2008; Carreras *et al.*, 2009).

Lichens were recognized as potential indicators of air pollution as early as the 1860s in Europe and elsewhere (Freitas, 1985; Freitas *et al.*, 1999; Gao, 1988; Garty *et al.*, 1993; Carreras *et al.*, 2009), and have since been increasingly used in air pollution studies. Lichens have a large surface area: volume ratio, a simple anatomy and lack a well developed root system (Aznar *et al.*, 2008); hence, they rely directly on atmospheric particulate deposition for nourishment (Loppi *et al.*, 1999; Carreras *et al.*, 2009) and, as a result, readily bioaccumulate pollutants from air (Ng *et al.*, 2005; Godinho *et al.*, 2008). Most importantly, lichens have the ability to reflect prevailing atmospheric metal ions pollutant levels in their tissues without significant adverse effects on their survival or growth (Adamo *et al.*, 2003; Ng *et al.*, 2005). Also, many lichens are geographically extensive in their distribution which facilitates biomonitoring programmes over extended areas (Ng *et al.*, 2005).

Furthermore, lichens can accumulate and retain many trace elements in concentrations that greatly exceed their physiological requirements (Aznar *et al.*, 2008) due to their relatively large surface area and slow growth (Carreras *et al.*, 2009). Lichens can tolerate these high concentrations by sequestering elements extracellularly as oxalate crystals or lichen acid complexes (Nieboer *et al.*, 1978; Loppi *et al.*, 1999; Carreras *et al.*, 2009). They can also record an integrated signal over a few years of atmospheric fallout and thus minimise any signals due to variable (seasonal) atmospheric circulation patterns, and biases related to isolated events (Aznar *et al.*, 2008). Hence, several papers have been published on monitoring trace and heavy metals using lichens in different geographic areas (e.g., Ng *et al.*, 2005; Aznar *et al.*, 2008; Godinho *et al.*, 2008, 2009; Policnik *et al.*, 2008; Carreras *et al.*, 2009).

Lichens accumulate substances from their environment by a variety of mechanisms. These mechanisms include particulate trapping, ion exchange, extracellular electrolyte sorption, hydrolysis and intracellular uptake (Nieboer *et al.*, 1978).

2.4.2 Sediments

Heavy metals discharge into a river system by natural or anthropogenic sources are distributed between the aqueous phase and bed sediments (Sin *et al.*, 2001). Sediment can provide a deeper insight into the long term pollution state of a water body (Awofolu *et al.*, 2005). The analysis of river sediments is a usefull method to study the metal pollution in an area (Sin *et al.*, 2001)

2.4.3 Water

Water samples are normally used in almost all pollution research on water bodies to quantify the various pollutants in such waters especially heavy metal studies. For instance, using water samples Aksoy *et al.* (2005) demonstrated high concentrations of heavy metals in waters of Sultan Marsh and its environs of Turkey. Through water sample analysis, Awofolu *et al.* (2005) reported the occurrence of toxic metals in Tyme river of South Africa. Aksoy *et al.* (2005) and Liua *et al.* (2002) reported that through atmospheric pollution, effluent discharges (from both domestic and industrial sources), use of agricultural chemicals, eroded soils, and domestic and industrial waste, water bodies have been the recipient of toxic substances including heavy metals.

2.4.4 Soil

The high levels of heavy metals and other pollutants in the soils have been attributed to metal rich source rocks, atmospheric pollution from motor vehicles, combustion of fossil fuels, agricultural fertilizers and pesticides, organic manures, disposal of urban and industrial wastes, as well as mining and smelting processes (Alloway, 1990; Brumelis *et al.*, 1999).

Findings from many studies on soil samples have reported high concentrations of heavy metals which are released into the environment (Moral *et al.*, 2005). Many soils in industrialized countries are affected by acid deposition, mine waste (containing toxic materials including heavy metals) and organic refuses, such as sewage sludge (Moral *et al.*, 2005).

2.5 AIR, WATER, AND SOIL QUALITY STANDARD

In pollution studies, measured concentrations of various pollutants in the atmosphere, water and soil are normally compared with established set of standards or guidelines of notable agencies. This comparison process enables researchers to evaluate the pollution status of any vicinity of interest. The standards and guidelines establish the threshold concentrations of the pollutants above which they may pose danger to the environment. These standards and guidelines may be national or internationally generated by a body of repute comprising experts of the field.

The national bodies and international agencies may include the Environmental Protection Agency (EPA) of the various countries, World Bank, International Atomic Energy Agency (IAEA), World Health Organization (WHO) and other environmentally conscious bodies. Table

2.1 and 2.2 are the guidelines values for drinking water quality and tentative soil quality criteria for some metals respectively.

Table 2.1: Guidelines for drinking water quality

	Maximum allowable concentration in drinking water [mg/L]			
	EU**	WHO***	UK*	USA**
Cadmium	0.005	0.003	0.001	0.005
Manganese	0.02	0.4	-	0.05
Arsenic	-	0.01	0.05	-
Aluminium	-	0.2	-	-
Antimony	-	0.02	-	-
Copper	-	2	-	-
Mercury	-	0.001	-	-

*Source: UK Environment agency (1996)

** Source: US EPA (2006)

***Source: World Health Organization (2004)

Table 2.2: Tentative soil Criteria

	Concentration [mg/kg dry weight]		
Element	A ^[1]	B ^[2]	C ^[3]
Arsenic	20	30	50
Cadmium	1	5	20
Chromium	100	250	800
Cobalt	20	50	300
Copper	50	100	500
Mercury	0.5	2	10
Nickel	50	100	500
Tin	20	50	300

^[1] Reference value for 'good' soil quality

^[2] Limiting value for soil quality having potential for harmful effects on human health or the environment and requiring further investigation.

^[3] Limiting value for heavily polluted soil requiring remedial investigations and cleanup.

Source: VROM (1983)

2.6 APPLICATION OF MULTIVARIATE STATISTICAL METHODS IN ENVIRONMENTAL MONITORING AND ASSESSMENT STUDIES

The understanding of the dynamics of pollution indicator parameters in an area has been enhanced with the application of basic and advanced statistical methods. In recent times, multivariate statistical methods such as principal component analysis (PCA) and cluster analysis (CA) are being used in the treatment of pollution data (Vega *et al.*, 1998; Hussain *et al.*, 2008; Zhang *et al.*, 2009). The application of different multivariate statistical techniques helps in the interpretation of complex data to better understand the environmental and ecological status of the studied areas. It also allows the identification of possible factors that influence environmental systems and offers a valuable tool for reliable environmental management (Simeonov *et al.*, 2003; Zhang *et al.*, 2009). Many studies related to these methods have been carried out. For example, Vega *et al.* (1998) and Zhang *et al.* (2009) used PCA and CA to classify sampling sites and identified the latent pollution sources. According to the above researches, it can be concluded that these methods could be used to assess the relationships between variables and possible pattern in distribution of measured data. Computer software programmes such as SPSS, STATISTICA, SAS and R (version 2.4 and current versions) can be used to explore environmental pollution data using PCA and CA.

2.6.1 Cluster analysis (CA)

According to Vega *et al.* (1998), cluster analysis is an unsupervised pattern recognition technique that uncovers intrinsic structure or underlying behaviour of a data set without making prior assumptions about the data, in order to classify the objects of the system into categories or

clusters based on their nearness or similarity. Cluster analysis (CA) is used to develop meaningful aggregations, or groups, of entities based on a large number of interdependent variables. The resulting clusters of objects exhibit high internal (within-cluster) homogeneity and high external (between clusters) heterogeneity (Vega *et al.*, 1998).

Of all cluster analysis, hierarchical agglomerative cluster is the most common approach. Hierarchical agglomerative cluster analysis indicates groupings of samples by linking inter-sample similarities and illustrates the overall similarity of variables in the data set (Vega *et al.*, 1998). In hierarchical cluster analysis the distance between samples is used as a measure of similarity. There are two types of cluster analysis: R- and Q-modes (Hussain *et al.*, 2008). The R-mode CA can be used to assess the affinity among environmental parameters or variables, and ultimately the sources and processes with which they are associated (Hussain *et al.*, 2008). Q-mode CA is also used to group sampling sites. Hierarchical agglomerative cluster analysis can be performed by first normalizing a given data set by means of techniques such as complete linkage (furthest neighbour), average linkage (between and within groups), weighted pair-group and Ward's methods. Using squared Euclidean distances as a measure of similarity, a dendrogram is generated defining clusters. Cluster analysis uses all the variance or information contained in the original data set (Vega *et al.*, 1998).

2.6.2 Principal component analysis (PCA)

PCA is a powerful tool applied to reduce the dimensionality of a data set by explaining the correlation among a large set of variables in terms of a small number of underlying factors or principal components, while retaining as much as possible the variability presented in the given

dataset (Vega *et al.*, 1998). This reduction is achieved by transforming the dataset into a new set of variables – the principal components (PCs), which are orthogonal (non-correlated) and are arranged in decreasing order of importance.

Mathematically, the PCs are computed from covariance or other cross-product matrix, which describes the dispersion of the multiple measured parameters to obtain Eigenvalues and eigenvectors. Principal components are the linear combinations of the original variables and the eigenvectors. The characteristic roots (Eigenvalues) of the PCs are a measure of their associated variances, and the sum of Eigenvalues coincides with the total number of variables. Correlation of PCs and original variables and the sum of Eigenvalues coincides with the total number of variables (Vega *et al.*, 1998). Correlation of PCs and original variables is given by loadings, and individual transformed observations are called scores. The R-mode and Q-mode are the two types of PCA.

2.7 INDICES FOR AIR, SOIL AND WATER POLLUTION ASSESSMENT

Among the commonly used methods in analyzing pollution intensity in the environments are the Contamination Factor (CF), Pollution Load Index (PLI), Geoaccumulation Index (Igeo) and Contamination degree (C_d). According to Tomlinson *et al.* (1980), indices enable quality of the environment to be easily understood by non-specialist. They are also used to compare the pollution status of different areas of the environment (Tomlinson *et al.*, 1980).

2.7.1 Pollution Load Index (PLI)

Pollution Load Index is used to find out the mutual pollution effect at different stations by the different elements in soils and sediments (El-Sammak and Abdul-Kassim, 1999). The PLI of a sampling point, community or an area is obtained by deriving Contamination Factors (CFs), using background concentrations or baseline or concentration of the element of interest in an unpolluted area (Tomlinson *et al.*, 1980; El-Sammak and Abdul-Kassim, 1999; Adomako *et al.*, 2008). The CF of an element is the ratio of its concentration in sample and base concentration.

A number of contamination factors will be derived for different metals at each sampling site, and a site's pollution load index may then be calculated by multiplying the contamination factors and deriving the N^{th} root of the N factors (Tomlinson *et al.*, 1980). Pollution Load Index value of 1 indicates heavy metal load close to the background level, and value above 1 indicates pollution (Tomlinson *et al.*, 1980; Cabrera *et al.*, 1999).

2.7.2 Geoaccumulation Index

The geoaccumulation index (Igeo) has been used since the late 1960s, and has been widely employed in European trace metal studies (Yaqin *et al.*, 2008). Originally used for bottom sediments, it has been successfully applied to the measurement of soil pollution (Cabrera *et al.*, 1999; Grzebisz *et al.*, 2002; Yagin *et al.*, 2008, Okweye *et al.*, 2009). The Igeo values enable the assessment of pollution by comparing current and pre-industrial concentrations, although it is not always easy to reach pre-industrial sediment layers (Yaqin *et al.*, 2008). Geoaccumulation Index is calculated using the formula;

$$I_{\text{geo}} = \text{Log}_2(C_n/1.5 \times B_n)$$

where C_n is the measured concentration of the element in soil or sediment,

B_n is the geochemical background value and 1.5 is a constant.

The constant 1.5 allows for analyses of natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences (Teng *et al.*, 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al.*, 2008).

The equation indicates that the index will be affected by the content of the samples and the geochemical background values. The world average shale, Earth's crust, and the world average soil are some of the materials often used to provide background values (Turekian and Wedepohl, 1961; Karbassi *et al.*, 2008; Yaqin *et al.*, 2008). The world average shale concentrations of elements of interest are either directly measured in texturally equivalent uncontaminated sediments or size fractions or taken from literature (Teng *et al.*, 2004).

The geoaccumulation index consists of 7 grades or classes (Grzebisz *et al.*, 2002; Lokeshwari and Chandrappa, 2007; Yaqin *et al.*, 2008) [Table 4.9]. Class 7 is an open class and comprises all values of the index higher than class 6. The elemental concentrations in class 7 may be hundredfold greater than the geochemical background value (Teng *et al.*, 2004; Lokeshwari and Chandrappa, 2007; Yaqin *et al.*, 2008).

2.7.3 Contamination degree

As reported by Teng *et al.* (2004), Contamination degree (C_d) is used to determine the excessive values of monitored elements in water bodies. It is calculated by the equation;

$$C_d = \sum C_f$$

where $C_f = (C_a/C_n) - 1$ = contamination factor for the i-th element,

C_a = analytical value of the i-th element (component),

and C_n = upper permissible limits of the element in drinking water.

2.7.4 Enrichment Factor

The degree of sediment and soil pollution may be evaluated using an Enrichment Factor (EF) [Karbassi *et al.*, 2008; Okweye *et al.*, 2009]. The EF compares present concentrations of elements to their background levels in shale. Enrichment Factor (EF) is computed for elements using:

$$EF = \{(C_n/CAI)_{\text{sample}}\} / \{(C_n/CAI)_{\text{crust}}\},$$

where $(C_n/CAI)_{\text{sample}}$ is the ratio of the concentration of the element of concern (C_n) to that of Al (CAI) in the sediment or soil sample,

and $(C_n/CAI)_{\text{crust}}$ is the same ratio in an unpolluted reference sample.

An EF value for an element between 5 and 10 is considered significantly enriched in the sample.

The EF values of 3-5 and <3 for an element are considered moderately enriched and depletion to minimal enrichment in the sample respectively (Okweye *et al.*, 2009).

2.8 PREVIOUS WORK ON HEAVY METAL POLLUTION IN THE STUDY AREA

Few works done on heavy metals at Teberbie and its environs include those reported by Akabzaa and Darimani (2001) and Asklund and Eldvall (2005). Water samples taken from Mile 7, Mile 8 and Teberbie, and analysed by the Environmental Chemistry Division of The Water

Research Institute of the Council for Scientific and Industrial Research (1998) yielded the results shown by Table 2.3.

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Table 2.3: Heavy metal levels (in mg/l) in borehole water samples from Mile 7, 8 and Teberebie.

Element	Mile 7 well	Mile 8 borehole	Teberebie borehole	Teberebie Stream
Zn	0.03	0.09	0.08	0.09
Pb	<0.01	0.01	<0.01	0.06
Cd	<0.01	<0.01	0.02	0.01
Mn	0.05	0.25	0.08	0.11
Fe	0.2	0.1	<0.01	<0.01
Cr	0.07	0.06	0.13	0.13
Ni	0.04	0.05	0.07	0.15
Co	0.14	0.06	0.11	0.13

Source: Akabzaa and Darimani (2001)

Borehole water samples from Mile 8 showed elevated manganese level (Asklund and Eldvall, 2005). The average manganese concentration in Mile 8 borehole water was 0.968mg/l which exceeded the WHO guideline value of 0.4mg/l in drinking water (Asklund and Eldvall, 2005). Other heavy metals (arsenic, cadmium, chromium, aluminium, cobalt and copper) studied by Asklund and Eldvall in Mile 8 and Teberebie boreholes were found to be less than the WHO guideline values.

CHAPTER THREE

MATERIALS AND METHODS

3.1 THE STUDY AREA

Teberebie, Miles 6, 7 and 8 which are part of the Tarkwa mining lease lands is located in the Wassa West District in the Western Region of Ghana with Tarkwa as the capital (Fig. 3.1). The district lies between latitudes 4° N and $5^{\circ} 40''$ N and longitudes $1^{\circ} 45''$ W and $2^{\circ} 10''$ W (Akabzaa and Darimani, 2001). It is bordered to the north by the Wassa Amenfi District, to the south by the Mpohor-Wassa East and Ahanta West, to the east by the Mpohor-Wassa East and to the west by the Nzema East District (Fig. 3.2). This area lies within the southwestern equatorial climate zone, where the seasons are primarily regulated by moist southwestern monsoon winds from the South Atlantic Ocean and dry, laden northeast trade winds, which blow over the Sahara desert from the northern subtropical high pressure zone (GFGL, 2007).

Rainfall usually peaks during two periods, April through June and October through November, with a mean annual rainfall of 1926mm. The abundance of rainfall and moderate temperatures in the area are conducive to dense vegetation growth. Relative humidity for the area does not vary remarkably throughout the year, ranging from 70% to 90%. The mean monthly temperatures are within the range of $24-28^{\circ}$ C. The lowest temperatures recorded for the area occur during July and August due to extensive cloud cover, while the highest monthly temperatures are usually recorded during February and March, when cloud cover is sparse (GFGL, 2007). The vegetation of the area consists of tropical rain forest characterized by rich undergrowth of climbers and

shrubs of varying heights. The trees, which generally reach heights of between 15 and 45 metres, are distributed mostly at the summit of hills where mining has not yet reached.

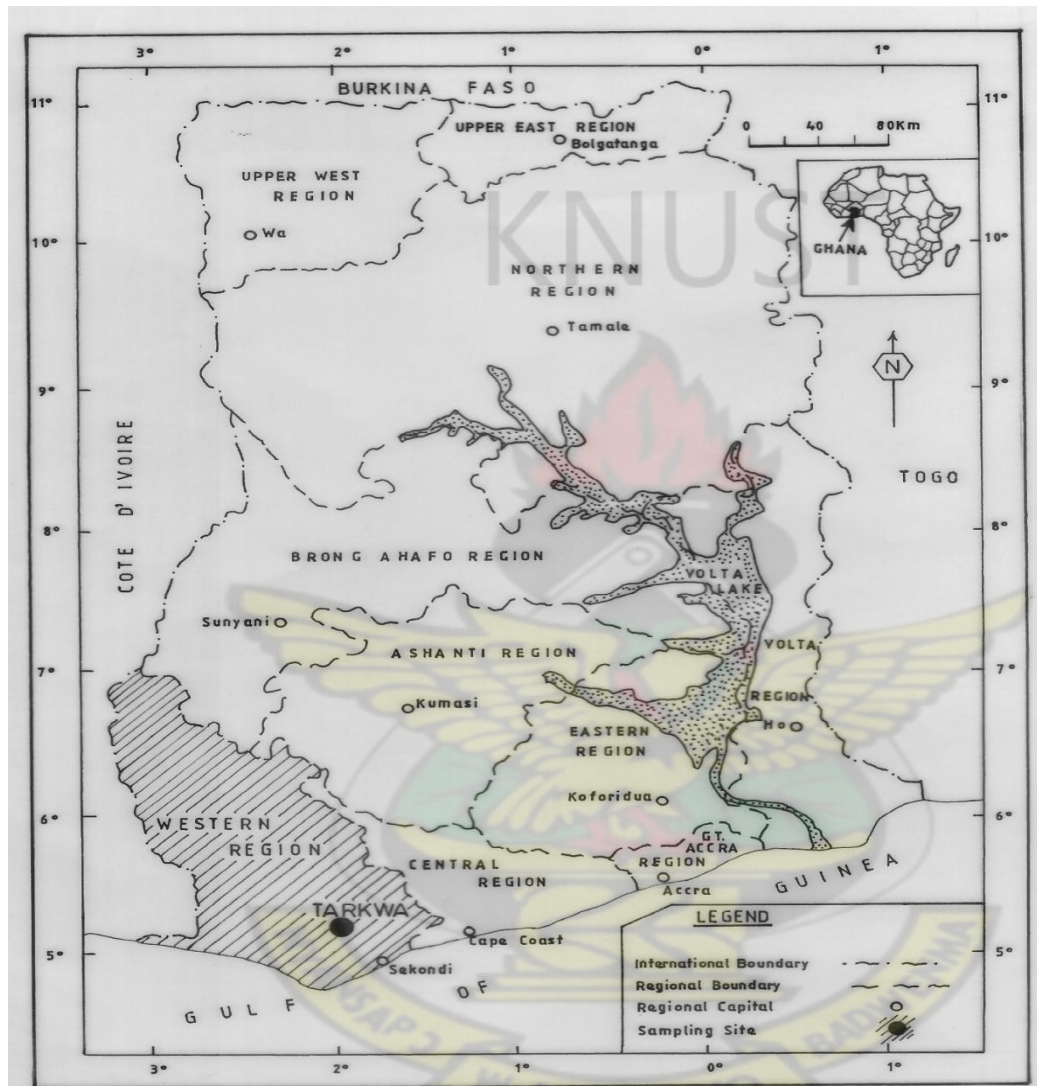


Fig.3.1: Map of Ghana showing Tarkwa

There has been a rapid reduction in the density of trees in areas affected by mining activities. Where the area has been mined out, the vegetation consists of ferns and other shrubs which grow profusely on the hilly slopes. The topography of the study area is characterized by ragged ridges with peaks reaching a height in some areas 335 metres above mean sea level, interspersed by

undulating valley bottoms. Teberebie and its environs have evergreen mountain ranges which are rich in biodiversity. Unfortunately, these ridges are the main areas where gold is found, and they are targets for open pit mines (Akabzaa and Darimani 2001).

The major rivers (Bediabewu, Drobo, Angonabeng and Bonsa) and their tributaries facilitate mining activities in the area, particularly for *galamsey* operators, by providing the water required for the processing of gold. In Wassa West district about 40% of the dwellers have access to pipe-borne water while about 25 % use rivers or streams as their source of water (ModernGhana.com, 2008). The study area has about 5 bore holes and no pipe borne water. Occasionally, especially during the dry season, some of the boreholes dry up and the inhabitants resort to the available streams for their water needs, including drinking. The two main large scale mines in the study area are Teberebie Goldfields Limited (TGL) which has been operating since 1990 and Iduapriem Anglogold Ashanti Mines (IAAM) which has also been operating since 1992 (Akabzaa and Darimani, 2001) .

3.2 SAMPLE COLLECTION AND PREPARATION

Samples of lichens, soils, sediments and water were collected from ten sampling points between September 2008–January 2009. Samples were collected once every month from all designated sampling points (Fig. 3.2). Sampling points were randomly selected from the four communities.

3.2.1 Lichen sampling and preparation

In situ lichens, identified as *Parmelia sp.*, were collected from sampling points 1, 2, 4, 5, 6, 7, 8, 9 and 10 located in and around Teberebie, Miles 6, 7 and 8 (Fig. 3.2). Lichen and soil samples

were also collected from an unpolluted environment (University of Cape Coast) to serve as control samples. About 55 samples of lichens were carefully collected from the barks of trees together with their substrates with the aid of a stainless steel knife at 1.5–2m above the ground (Plate 1). The samples were collected at about 1.5M above the ground following Nyarko *et al.* (2004) methodology to avoid contamination from soil particles.



Plate 1. Lichen (*Permalia sp*) sampling from a tree bark.

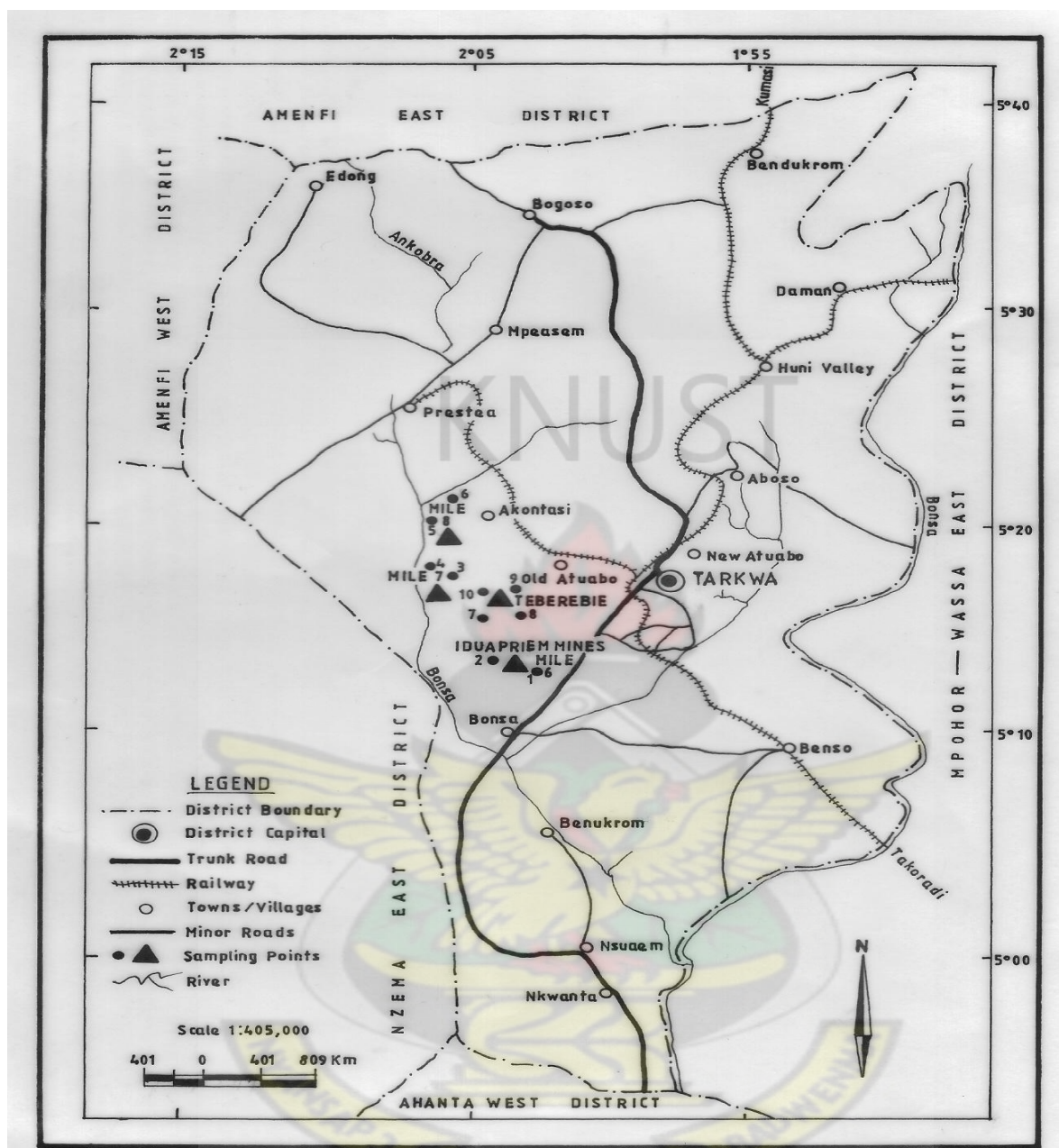


Fig.3.2: Map of study area showing sampling sites.

The collected samples were neatly packed into polyethylene bags and transported to the laboratory for preparation and subsequent analysis. In the laboratory, any adhered foreign material was manually removed. The lichens were washed for about 60 seconds in de-ionized water to remove dust and sand, air dried on clean transparent polythene sheets at room

temperature for 48 hours. The dried lichen samples were carefully scrapped from the adhering tree barks (substrates) using lancets, ground into powder using agate mortar and pestle and homogenized. Six sub-samples each with a mass of 200mg were weighed onto polythene films, wrapped and heat-sealed for short and medium term irradiations. The packaged lichens were placed into plastic polyethylene vials and heat-sealed for Thermal Instrumental Neutron Activation Analysis (TINAA).

3.2.2 Soil sampling and preparation

The soil samples from sampling points 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 located in and around Teberbie, Mile 6, 7 and 8 were collected at a depth of about 10-20cm using method of Teng *et al.* (2004). The soil samples were kept in polyethylene bags which had been rinsed with 1M HCl and dried and transported to the laboratory.

The samples were disaggregated, dried in a dry and dust-free place at room temperature for 3 days and ground. The samples were sieved using <40 mesh, homogenized and packed in polyethylene bags and stored in the laboratory until analysis. About 0.1g of each soil sample was weighed onto different polythene films wrapped and heat-sealed. Six replicate sub-samples were prepared for each sample, put into polyethylene irradiation capsules and heat-sealed for irradiation and analysis.

3.2.3 Water sampling and preparation

Water samples of rivers, springs and boreholes were taken from sampling points 3, 4, 7, 8, 9 and 10, as indicated by Fig. 3.3. River water samples were collected from downstream and

downslope. The collection of water samples of the river and springs was performed wearing polyethylene gloves, and facing the direction of flow of the stream. Pre-cleaned polyethylene 1litre sampling bottles were used for collection of the water. At each sampling point, the bottles were rinsed 3 times with the water before collection of the sample. Each bottle was immersed at about 8cm below the water surface.

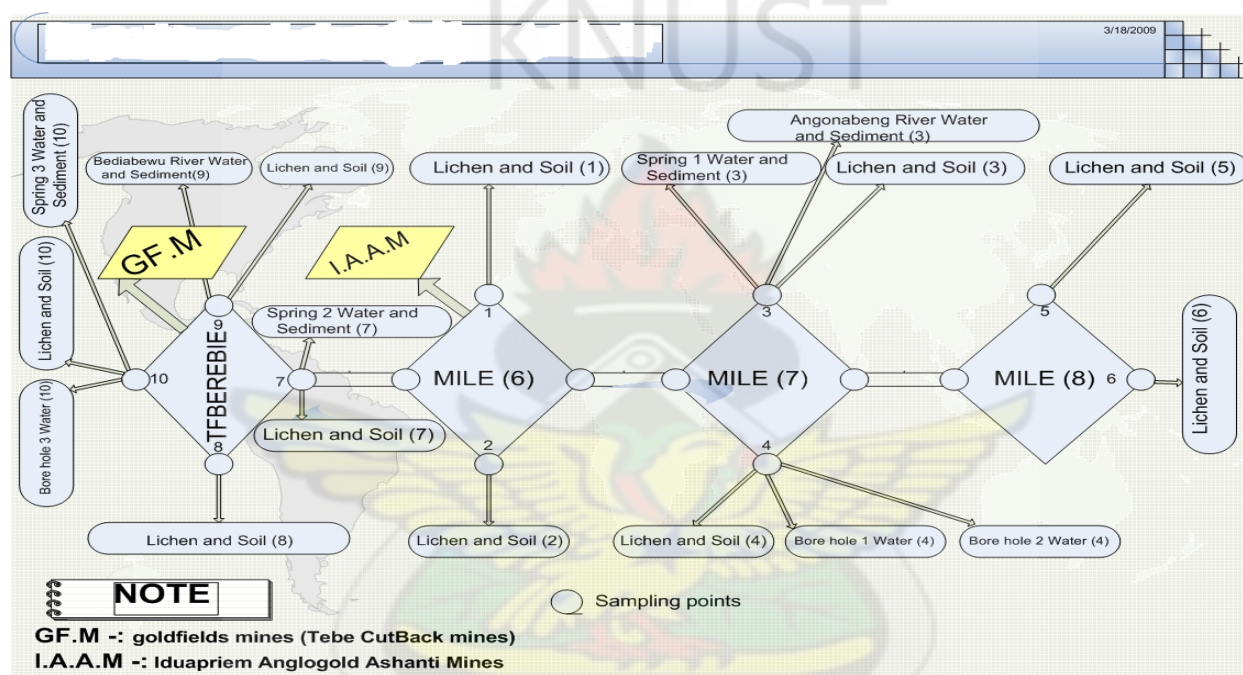


Fig.3.3: Sampling points, sample types, communities and the two main mines.

As shown on the sampling design (Fig. 3.3), water from streams and sediment samples, comprising three springs and two rivers were analyzed for their pollution load. Water and sediment samples were taken from Mile 7 (one spring and Angonabeng river) and Teberebie (2 springs and Bediabewu river). Water and sediment samples from Kakum river, which has no record of pollution and sprang through non mining towns and communities in the central region of Ghana were taken and analyzed to serve as a reference.

The water samples were acidified with 50% HNO₃ to achieve a pH of 2.0. The addition of acid to water sample is to keep the metal ions in the dissolved state, as well as to prevent microbial activities (Serfor-Armah *et al.*, 2006). The samples were then kept in an ice chest loaded with ice blocks, transported to the laboratory and stored in a refrigerator until they were analysed.

The borehole samples were carefully taken from the mouth and kept in clean 1litre sampling bottles which had been thoroughly rinsed with water. Sample treatment, transport and storage followed the same procedure described above for surface water samples.

Exactly 0.5ml of each water sample was pipetted using Eppendorf tip ejector pipette into clean pre-weighed 1.5ml polyethylene capsules and sealed. Two of these sample vials were placed into a 7.0ml polyethylene capsule and heat-sealed for medium irradiations. For short irradiations, only one of these sample vials was placed into a 7.0ml polyethylene capsule and loaded with cotton wool, and heat-sealed.

3.2.4 Sediment sampling and preparation

Sediments were collected from sampling points 3, 7, 8, 9 and 10 as shown in Fig. 3.3. Sediment samples at a depth of about 10cm were collected with a pre-cleaned plastic shovel. The plastic shovel was used to scoop the sediment. The sediment samples were transferred into pre-cleaned polyethylene bags. They were then transported to the laboratory.

In the laboratory, each sediment sample was air dried at room temperature for 3 days. Using polyethylene gloves, organic debris and other unwanted large particles were hand picked from

each sample. The dried samples were then sieved using 2 mm sieve and homogenized. Exactly 0.1g of each sediment sample was weighed onto polyethylene film, wrapped and heat-sealed. Six replicate sub-samples were prepared for each sample, packed into polyethylene irradiation vial and heat-sealed.

3.2.5 Standard sample preparation

The reference materials International Atomic Energy Agency (IAEA) -SOIL-7, IAEA-405 and IAEA-LICHEN-336 were used for quality control test and quantitative analyses. Six replicate samples each with a mass of 0.1 g, 0.1 g and 0.2 g of IAEA-SOIL-7, IAEA-405 and IAEA-LICHEN-336 respectively were weighed and heat-sealed in a similar manner as the soil and lichen samples.

3.3 SAMPLE IRRADIATION AND COUNTING

The samples and standards were irradiated using Ghana Research Reactor-1 (GHARR-1) facility at National Nuclear Research Institute laboratory of Ghana atomic Energy Commission (GAEC). GHARR-1 reactor (miniature neutron source) operated at power rating of 15 kW with a thermal neutron flux of $5.0 \times 10^{11} \text{ ns}^{-1} \text{ cm}^{-2}$. By means of pneumatic transfer systems which operated at a pressure of 1.723 bar, the samples were transferred into the inner irradiation sites. The scheme for irradiation was chosen according to the half-lives of the elements of interest. The soil, sediment and standards were short irradiated for 10 s. The lichens and water samples were irradiated for 120 s and 1 hr for short and medium irradiations, respectively. At the end of each irradiation, the samples were returned from the reactor and allowed to cool down until the level of activity was within the acceptable limit for handling. The irradiated samples were placed on

top of the detector and counts were accumulated for pre-selected time to obtain the spectra intensities. Ten minutes counting time was chosen for short and medium irradiations as done by Nyarko *et al.* (2004)

3.4 QUALITATIVE AND QUANTITATIVE ANALYSIS

The qualitative and quantitative measurements of elements in samples were performed using a PC-based gamma ray spectroscopy consisting of n-type high purity germanium (HPGe) detector model GR 2518 (Canberra industries Inc.), HV power supply model 3103, amplifier model 2020, an 8K Ortec multi-channel buffer (MCB) emulation software card and a Pentium II computer for spectrum and data evaluation and analysis. The detector had a relative efficiency of 25% to NaI detector and operated on a bias voltage of (–ve) 3000V with a resolution of 1.8keV for ^{60}Co gamma-ray energy of 1332 keV. The MCB card was used to obtain the spectra intensities of the samples. Microsoft windows based software MAESTRO was used for spectrum analysis (i.e., qualitative and quantitative analyses). The nuclear data which was used for the determination of the various elements in this study have been summarized in Table 3.1.

Table 3.1: Nuclear data of the elements used in NAA analysis

Element	Isotope produced	Gamma ray energy/keV	Half-life	Irradiation time(Ti)-A*	Irradiation time(Ti)-B*	Counting Time (Tc)
Sb	Sb^{122}	564.2	2.7days	1 hr	1 hr	600s
Mn	Mn^{56}	1811.4	2.58hrs	10s	120s	600s
Cu	Cu^{66}	1039.2	5.1mins	10s	120s	600s
V	V^{52}	1434.1	3.75mins	10s	120s	600s
Al	Al^{28}	1778.9	2.24mins	10s	120s	600s
Co	Co^{60}	1332.5	5.27yrs	1 hr	1 hr	600s
Hg	Hg^{197}	77.4	64.1hrs	1 hr	1 hr	600s
As	As^{76}	559.1	26.32hrs	1 hr	1 hr	600s
Cd	$\text{In}^{115\text{m}}$	336.3	53.5hrs	1 hr	1 hr	600s
Th	Th^{133}	86.5	22.3min	10s	120s	600s

NB: A* and B* are Ti for soil and sediment, and lichen and water respectively.

Source: Dampare *et al.* (2006); Adomako *et al.* (2008); Tando *et al.* (2009)

3.5 VALIDATION OF ANALYTICAL METHOD

The accuracy of the analytical method were evaluated using IAEA-405 (Trace elements and methylmercury in estuarine sediment) as certified reference material. The analytical values of the reference material obtained from this study were compared with the actual values (in ppm).

3.6 STATISTICAL ANALYSES AND CALCULATION OF POLLUTION INDICES

3.6.1 Statistical analyses

Mean and standard deviation of lichen, soil, and stream data were determined using SPSS version 16 software. The interrelationships among elemental concentrations in lichen, soil and stream samples were analysed using Spearman's and Pearson's correlation methods of the SPSS version 16 software.

Cluster analysis (CA) and principal component analysis (PCA), and charts (line and bar graphs) for lichen and soil data were performed using SPSS version 16 software. The lichen and soil data were normalized using Ward's method of linkage with squared Euclidean distance as a measure of similarity (Vega *et al.*, 1998; Zhang *et al.*, 2009).

Cluster analysis in R-mode was performed on all the examined elements (Sb, Mn, Cu, V, Al, Co, Hg, As, Cd and Th) in lichen and soil samples. Q-mode CA was used to define groups (clusters) of sampling points of a particular air or soil quality in terms of the examined elements (Chandrasekhran *et al.*, 2001; Grande *et al.*, 2003; Hussain *et al.*, 2008).

3.6.2. Calculation of pollution indices

The pollution Load Index (PLI), Geoaccumulation Index (Igeo), Enrichment Factor (EF) and Contamination degree (C_d) were computed using Microsoft Excel 2007 version.

3.6.2.1 Pollution Index Factor (PIF) or Contamination Factor (CF) for lichen, soil and sediment samples.

Air, soil and stream sediment pollution status of the study area were quantified using the Pollution Index Factor (PIF) approach as by Freitas and Nobre (1997) and Nyarko *et al.* (2004).

The equation used is given by;

$$PIF = C_s / C_c,$$

where C_s is the average concentration of element in the sample,

and C_c is the average concentration of element in lichen control samples or world average shale value for soils and sediments.

Tomlinson *et al.* (1980) and Cabrera *et al.* (1999) method was used in computing the overall pollution load indices (PLIs) of lichen, soil and sediment samples for the sampling points and communities. The PLI was evaluated using the equations below:

For sampling points:

$$PLI_{\text{sampling site}} = (CF_{Sb} \times CF_{Mn} \times CF_{Cu} \times CF_V \times CF_{Al} \times CF_{Co} \times CF_{Hg} \times CF_{As} \times CF_{Cd} \times CF_{Th})^{1/10}$$

For communities:

$$PLI_{\text{community}} = (PLI_1 \times PLI_2 \times \dots \times PLI_n)^{1/n}$$

where n = number of sampling points for a community,

CF = Contamination factor.

The PLI (for lichen and soil samples) for Mile 6, Mile 7 and Mile 8 was computed by taking the squared root of the product of the PLI of the sampling points in each community as done by Tomlinson *et al.* (1980). The PLI of Teberebie community was calculated by taking the 4th root of the product of the PLIs of sampling points SPSL7, SPSL8, SPSL9 and SPSL10.

Geoaccumulation Index (Igeo) approach was used to quantify the degree of anthropogenic contamination in soils and stream sediments. The Igeo for each element was calculated using the formula;

$$I_{geo} = \text{Log}_2(C_n/1.5 \times B_n),$$

where Igeo is the Geoaccumulation Index,

C_n is the measured element concentration in soil or sediment sample,

and B_n is the geochemical background value in world average shale.

The Enrichment Factor (EF) in soil and stream sediment samples was computed for elements and each sampling point using:

$$EF = [(C_n/CAI)_{\text{sample}}]/[(C_n/CAI)_{\text{shale}}],$$

where (C_n/CAI)_{sample} is the ratio of the concentration of the element of concern (C_n) to that of Al (CAI) in soil or sediment sample,

and (C_n/CAI)_{shale} is the same ratio in world average shale value.

3.6.2 Lichen samples contamination analysis using Enrichment Factor (EF) and Estimated Background Concentration (EC)

In order to evaluate the incidence of soil contamination of lichen samples, Enrichment Factor (EF) and Estimated Background Concentration (EC) methods of Bargagli (1995) and Loppi *et al.* (1999) were used. The EF method is based on the normalization of elements in soils by calculating Enrichment Factors (EFs) for each element (Loppi *et al.*, 1999) according to the formula:

$$EF = (X_L/R_L) / (X_S/R_S),$$

where X_L is the element in question in the lichen,

R_L is the reference element in the lichen, X_S is the element in question in the soil and R_S is the reference element in the soil.

Aluminium which is a principal element in the Earth's crust and has limited metabolic significant is commonly used as an indicator of sample contamination by wind-borne soil and rock dust (Bargagli, 1995; Loppi *et al.*, 1999). Hence, in this study, Al was selected as a reference element to normalize and correct for soil contamination of lichen samples.

The EC method involved the calculation of estimated background element concentrations in lichen samples by ascribing the excess of a reference element to soil contamination (Bargagli, 1995), according to the formula:

$$X_{LE} = X_L - \{X_S[(R_L - B_L)/R_S]\},$$

where X_{LE} is the estimated concentration of the element in question in the lichen,

X_L the element in question in the lichen,

X_S the element in question in soil, R_L the reference element in the lichen,

and B_L the background of the reference element in the lichen and R_S the reference element in the soil.

3.6.3 Calculation of Contamination degree (C_d) of Stream water.

To assess the excessive values of monitored elements in water samples, the Teng *et al.* (2004) approach was followed using the equation:

$$C_d = \sum C_{f_i},$$

where C_d is the contamination degree,

and C_{f_i} is the contamination factor for the i -th element,

$$C_{f_i} = (C_n/C_b) - 1,$$

where, C_n is the analytical value of the i -th element,

and C_b is the upper permissible limit of element in water.

In this study, the WHO (2004) guideline values for drinking water quality was selected for the calculation of contamination degrees of the water from streams.

CHAPTER FOUR

RESULTS

4.1 QUALITY CONTROL FOR ELEMENTAL ANALYSIS

The analytical results obtained at GHARR-1 laboratory for the reference material IAEA-405 compared with certified values are shown in Table 4.1. The values compare favourably well with the recommended values for Sb, Mn, Cu, V, Al, Hg, Cd, Co, As and Th with bias less than 6%. The precision was calculated as a percentage relative standard deviation (%RSD) of six replicate samples of the prepared standard, and was found to be less than 5%.

Table 4.1: Analytical results (in ppm) of Standard Reference Material, IAEA-405 (Estuarine sediment), showing local laboratory values and recommended values.

Analyte	This work	Certified value	Bias	%RSD
Sb	1.73±0.02	1.81	-0.080	1.156
Mn	498±2.1	495	3.000	0.422
Cu	47.7±0.11	47.7	0.000	0.231
V	91.2±0.87	95	-3.800	0.954
Al	75641±25.1	77900	-2259.000	0.033
Co	13.9±0.03	13.7	0.200	0.216
Hg	0.79±0.02	0.81	-0.020	2.532
As	23.1±0.15	23.6	-0.500	0.649
Cd	0.7±0.01	0.73	-0.030	1.429
Th	16.01±0.2	14.3	1.710	1.249

4.2 LICHENS

4.2.1 Elements accumulation in lichen *Parmelia sulcata*

The results of the Instrumental Neutron Activation Analysis (INAA) measurements (ppm, dry weight) of Sb, Mn, Cu, V, Al, Co, Hg, As, Cd and Th in *Parmelia sulcata* samples from Mile 6,

Mile 7, Mile 8 and Teberebie as well as the control site are presented in Table 4.2. The average concentrations of the elements in lichen samples from the communities are given in Appendix 2.

Variations in elemental contents in lichens at the various sampling sites are shown by Appendix 1.

Table 4.2: Average INAA values of heavy metals (ppm/dry weight) in lichens

	Mile 6		Mile 7		Mile 8		Teberebie				CONTROL
	SPLCH1	SPLCH2	SPLCH3	SPLCH4	SPLCH5	SPLCH6	SPLCH7	SPLCH8	SPLCH9	SPLCH10	CONTRL
Sb	0.85	4.75	0.78	2.03	1.05	0.89	10.35	1.19	5.59	2.97	0.16
	<i>1.30</i>	<i>7.67</i>	<i>0.83</i>	<i>2.39</i>	<i>0.16</i>	<i>0.56</i>	<i>6.17</i>	<i>2.28</i>	<i>7.01</i>	<i>3.90</i>	<i>0.10</i>
Mn	1097	158	178	560	51.1	37.1	238	239	386	782	144
	<i>1383</i>	<i>85.1</i>	<i>248</i>	<i>928</i>	<i>10.8</i>	<i>10.0</i>	<i>87.9</i>	<i>74.5</i>	<i>7.06</i>	<i>1321</i>	<i>22.3</i>
Cu	0.26	0.51	2.21	1.19	0.60	0.31	370	2.58	4.75	4.98	1.23
	<i>0.56</i>	<i>0.57</i>	<i>1.58</i>	<i>1.28</i>	<i>0.42</i>	<i>0.15</i>	<i>497</i>	<i>1.48</i>	<i>8.12</i>	<i>7.61</i>	<i>0.01</i>
V	5.79	4.84	5.98	8.10	3.20	1.53	27.24	9.08	21.57	12.14	0.300
	<i>2.50</i>	<i>0.62</i>	<i>0.48</i>	<i>1.28</i>	<i>0.29</i>	<i>0.38</i>	<i>14.4</i>	<i>2.51</i>	<i>16.29</i>	<i>3.57</i>	<i>0.31</i>
Al	15.71	14.78	11.61	16.20	10.87	8.38	42.78	20.36	69.55	19.00	8.00
	<i>5.70</i>	<i>1.59</i>	<i>0.34</i>	<i>3.75</i>	<i>0.80</i>	<i>1.25</i>	<i>22.7</i>	<i>2.40</i>	<i>5.84</i>	<i>1.47</i>	<i>10.5</i>
Co	1.02	0.87	0.17	0.48	0.22	0.12	0.9	6.13	1.17	0.41	0.37
	<i>1.00</i>	<i>1.27</i>	<i>0.23</i>	<i>0.02</i>	<i>0.40</i>	<i>0.05</i>	<i>1.24</i>	<i>4.63</i>	<i>1.57</i>	<i>0.34</i>	<i>0.02</i>
Hg	1.24	1.00	0.76	0.24	ND	ND	0.48	0.16	0.61	0.37	ND
	<i>1.10</i>	<i>1.10</i>	<i>0.41</i>	<i>0.12</i>	-	-	<i>0.23</i>	<i>0.12</i>	<i>0.26</i>	<i>0.31</i>	-
As	8.00	2.25	0.25	0.28	0.26	0.27	0.39	0.25	0.25	0.43	0.10
	<i>8.10</i>	<i>2.20</i>	<i>0.10</i>	<i>0.20</i>	<i>0.16</i>	<i>0.10</i>	<i>0.28</i>	<i>0.12</i>	<i>0.10</i>	<i>0.28</i>	<i>0.01</i>
Cd	1.02	0.83	0.58	0.38	0.53	0.26	1.41	0.99	0.39	1.03	ND
	<i>0.92</i>	<i>0.37</i>	<i>0.24</i>	<i>0.31</i>	<i>0.68</i>	<i>0.41</i>	<i>0.37</i>	<i>0.67</i>	<i>0.15</i>	<i>1.21</i>	-
Th	0.12	0.01	0.21	0.15	0.10	0.11	0.03	0.01	0.01	0.01	ND
	<i>0.24</i>	<i>0.01</i>	<i>0.17</i>	<i>0.01</i>	<i>0.07</i>	<i>0.11</i>	<i>0.04</i>	<i>0.001</i>	<i>0.001</i>	<i>0.01</i>	-

ND implies below detection limit

Concentrations in italics represent standard errors

The range of Sb concentrations in lichens across the communities ranged between 0.78 and 10.35ppm. The sampling point 7 (SPLCH7) at Teberebie recorded the highest average Sb concentration of 10.35ppm whilst sampling point 3 (SPLCH3) at Mile 7 registered the least average Sb level of 0.78ppm and the control site had 0.16ppm. Average Mn levels in lichens from the studied area ranged between 37.1 and 1097ppm. The highest average Mn concentration

(1097ppm) in lichens occurred at sampling point 1 (SPLCH1) at Mile 6 and the lowest (37.1ppm) was observed at sampling point 6 (SPLCH6) at Mile 8.

The highest average Cu concentration of 370ppm in lichens occurred at sampling point 7 whereas the sampling point 1 recorded the least value of 0.26ppm. The sampling points 2, 5 and 6 had average Cu concentrations in lichens less than 1ppm. The highest average V concentration of 27.24ppm in lichens occurred at sampling point 7 and sampling point 6 had the lowest value of 1.53ppm. The Al concentrations in lichen samples from Mile 6, 7, 8 and Teberebie were between 69.55 and 8.38ppm. Generally, sampling points at Teberebie recorded the highest values of Al concentration whereas Mile 8 sampling points registered the least concentrations. The Co concentrations in the lichen samples were in the range of 0.12 – 6.13ppm. The sampling point 8 (SPLCH8) at Teberebie recorded the highest level of Co in lichen of 6.13 while sampling point 6 (SPLCH6) at Mile 8 had the least value of 0.12ppm. Sampling points SPLCH2, SPLCH3, SPLCH4, SPLCH5, SPLCH6, SPLCH7 and SPLCH10 recorded average Co concentrations less than 1ppm.

Mile 6 registered the highest Hg concentration of 1.24ppm (SPLCH1). Mile 7 (SPLCH3) and Teberebie (SPLCH 6 to 10) had Hg levels in lichens less than 1ppm whereas the Hg levels in lichens at Mile 8 (SPLCH5 and SPLCH6) were less than the detection limit. The highest average As concentrations (8ppm) occurred at Mile 6 (SPLCH1 and SPLCH2) while the rest of the communities recorded values less than 1ppm. The lowest average As concentration of 0.25ppm occurred at sampling points SPLCH3, SPLCH8 and SPLCH9.

Cadmium concentrations in lichens ranged between 0.26 and 1.41ppm. Sampling point 7 (SPLCH7) at Teberebie recorded the highest value and sampling point 6 (SPLCH6) at Mile 8 had the least average concentration. The average Th concentrations in the lichen samples across the sampling points were all found to be less than 0.25ppm.

4.2.2 Pollution Index Factor (PIF) or Contamination Factor (CF) for lichen samples

The Pollution Index Factor (PIF) or Contamination Factor (CF) ranges, pollution grades and their corresponding status according to Nyarko *et al.* (2004) are given in Table 4.3. The PIF and Pollution Load Index (PLI) values of the elements in the analysed lichens from all the sampling points in the study area are given in Table 4.4. Sampling point 7 had the highest Sb Contamination Factor (CF) value of 51.73 and sampling point 3 had the lowest value of 4.96. The highest CF value (7.61) of Mn occurred at sampling point 1 and the least value (0.26) was recorded at sampling point 6 (SPLCH6) at Mile 8. Sampling point 1, 2, 4, 5 and 6 registered CF values for copper (Cu) less than 1.0. However, all Teberebie sampling points (7, 8, 9 and 10) had CF values for Cu in the range between 2.1 and 4.1. Sampling point 7 had the highest CF value for vanadium (V) of 70.76 and sampling point 6 had the least value of 3.98. The highest CF value of 8.69 for Al occurred at sampling point 9 and the lowest value (1.05) was recorded at sampling point 6. Sampling point 8 had the highest CF value of 16.57 for Co and sampling point 6 had the least value of 0.32. The contamination factor for Hg was the highest among the monitored elements. Sampling point 1 of Mile 6 had the highest CF value of 622 for Hg and all the two sampling points (SPLCH 5 and 6) at Mile 8 recorded values less than 0.05. Sampling point 1 had the highest As CF value of 80 while sampling point 3, 4, 5, 6, 8, and 9 recorded values between 2 and 3. The highest Cd CF value (14.08) occurred at sampling point 7 and the

lowest value (2.62) was registered at sampling point 6. All the sampling points had Th CF values less than 0.7.

Teberebie recorded the highest PLI value of 6.00 and Mile 8 had the least value of 0.88 (Fig. 4.1). The sequence of PLI values of the studied communities is as follows; Teberebie (6.00) > Mile 6 (5.18) > Mile 7 (3.88) > Mile 8 (0.88).

Table 4.3: PIF ranges and their designated pollution grade and intensity.

PIF	GRADE	INTENSITY
<1.2	I	Unpolluted area
1.2–2	II	Light polluted area
2–3	III	Medium polluted area
>3	IV	Heavily polluted area

Source: Nyarko et al. (2004)

Table 4.4: *Parmelia* lichens and their Pollution Index Factors and PLI for sampling points

	Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th	PLI
SPLCH 1	5.35	7.61	0.21	15.04	1.96	2.57	622	80	10.24	0.34	6.38
SPLCH 2	30.08	1.09	0.41	12.56	1.85	2.36	498	22.48	8.30	0.03	4.28
SPLCH 3	4.96	1.23	1.80	15.54	1.45	0.47	378	2.48	5.84	0.63	3.63
SPLCH 4	12.87	3.88	0.96	21.04	2.02	1.29	120	2.82	3.82	0.44	4.14
SPLCH 5	6.64	0.35	0.49	8.22	1.36	0.59	<0.05	2.6	5.34	0.28	1.04
SPLCH 6	5.61	0.26	0.25	3.98	1.05	0.32	<0.05	2.72	2.62	0.31	0.75
SPLCH 7	51.73	1.65	301	70.76	5.34	2.44	239	3.68	14.08	0.08	10.89
SPLCH 8	7.56	1.65	2.10	23.59	2.54	16.57	81	2.54	9.86	0.03	4.17
SPLCH 9	35.41	2.68	3.86	56.02	8.69	3.15	305	2.48	3.96	0.03	5.89
SPLCH10	18.8	5.00	4.10	31.52	2.00	1.11	184	4.28	10.34	0.03	4.81

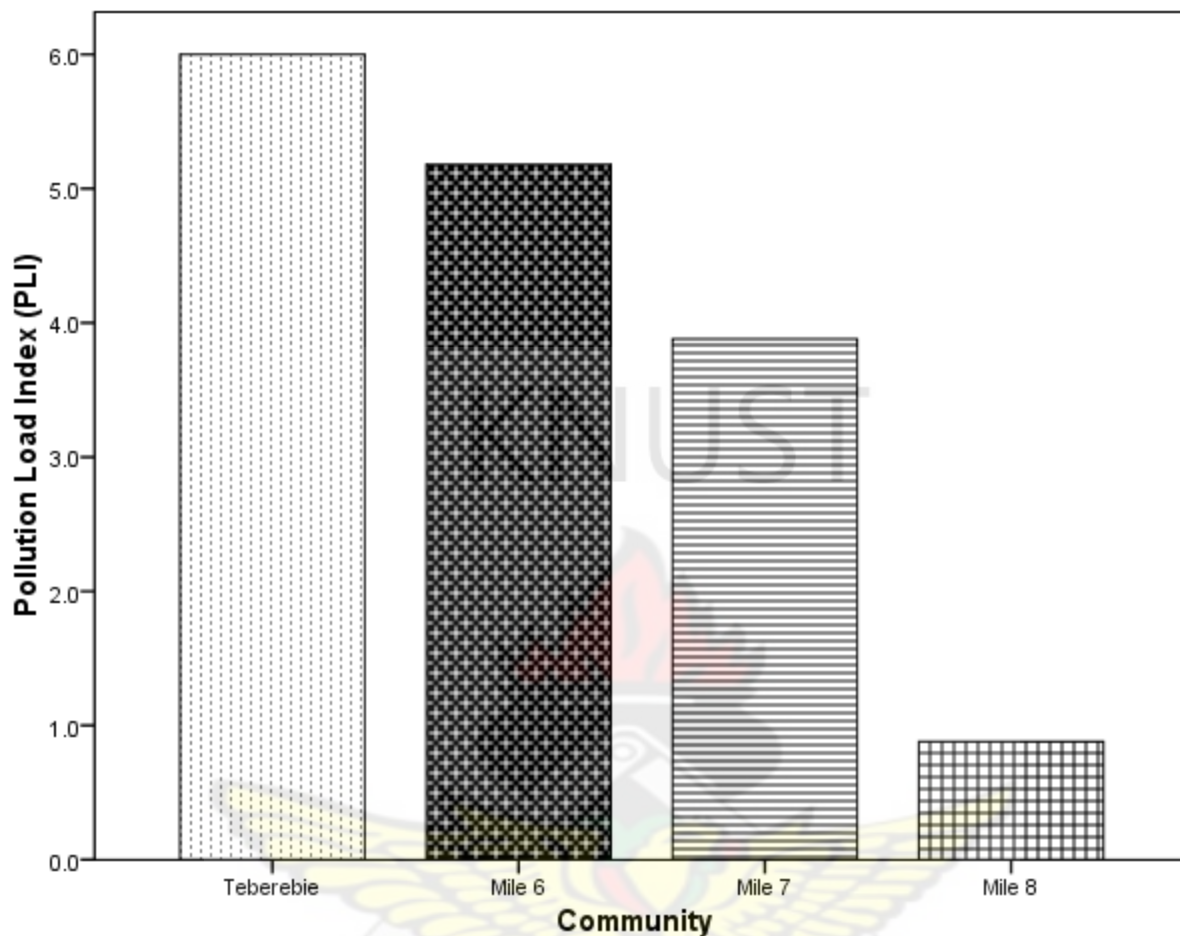


Fig. 4.1: A comparison of PLI values for lichens in communities of the study area.

4.2.3 Principal component analysis (PCA) of lichen data

(a) R-mode principal component analysis of element levels in lichens

The results of the R-mode PCA are presented in Table 4.5 with significant factor loadings in bold faced. Three principal components were obtained with Eigenvalues > 1 , explaining 87.4% of the total variance in lichen dataset.

Table 4.5: Rotated component matrix of 3 factor model explaining 87.4% of the total variance for lichens

	PC1	PC2	PC3	Communalities
Sb	0.830	0.358	0.206	0.859
Mn	0.273	-0.023	0.857	0.810
Cu	0.894	-0.105	-0.094	0.819
V	0.819	0.447	0.339	0.986
Al	0.900	0.027	0.330	0.920
Co	0.565	-0.224	0.644	0.784
Hg	0.468	0.479	0.662	0.887
As	-0.254	0.446	0.746	0.819
Cd	0.351	0.874	0.227	0.938
Th	-0.071	0.957	-0.049	0.923
Eigenvalue	3.775	2.498	2.473	
% of total variance	37.746	24.975	24.727	
Cummulative % of variance	37.746	62.722	87.449	

The first principal component (PC1), accounting for 37.746% of the total variance, was correlated with Sb, Cu, V, Al and Co. The second principal component (PC2), explaining 24.975% of the total variance, was correlated primarily with Cd and Th. The third principal component (PC3), accounting for 24.727% of the total variance, was weighted on Mn, Co, Hg, and As.

(b) Q-Mode principal component analysis of sampling points

Using Q-mode PCA, the sampling sites were classified according to the concentrations of elements present in the 3 PCs given in Table 4.5. The factor scores for the three principal components identified in Table 4.5 are shown by Table 4.6.

For PC1, the elements Sb, Cu, V, Al and Co are highly concentrated at SPLCH7, SPLCH9 and SPLCH10 with factor scores 1.63666, 1.04649 and 1.51307 respectively (Table 4.6). The PC2 represents strong correlation for Cd and Th at the following sampling points in the order; SPLCH3>SPLCH6>SPLCH1>SPLCH5>SPLCH4>SPLCH2. PC3 showed strong correlation for the elements Mn, Co, Hg and As at sampling points SPLCH1 and SPLCH2.

Fig. 4.2 shows the factor scores of sampling points on the bidimensional plane defined by PC1 and PC2. This plot puts 11 sampling points (including control) into 2 dimensions explaining 67.722% of the total variance. Samples from Mile 6, Mile 7 and Mile 8 (SPLCH1, SPLCH2, SPLCH3, SPLCH4, SPLCH5, and SPLCH6) are distinctly separated from the lichen samples from Teberebie (SPLCH7, SPLCH8, SPLCH9, and SPLCH10). Fig. 4.3 also shows the scores of sampling points on the bidimensional plane defined by PC1 and PC3. This plot puts 11 sampling points (including control) into 2 dimensions explaining 62.473% of the total variance. Similarly, lichens from Mile 6, Mile 7 and Mile 8 are distinguished from the lichens of Teberebie in the plot of PC1 versus PC3.

Table 4.6: Varimax rotation factor scores for the 3 factor model for the analysed lichens

	PC1	PC2	PC3
SPLCH 1	-1.24642	0.61214	2.07857
SPLCH 2	-0.43890	0.34181	0.74589
SPLCH 3	-0.33131	0.83160	-0.55855
SPLCH 4	-0.14107	0.42293	0.17516
SPLCH 5	-0.51553	0.60884	-1.28417
SPLCH 6	-0.87938	0.66039	-1.45754
SPLCH 7	1.63666	0.25848	-0.50204
SPLCH 8	0.31646	-0.44382	0.45536
SPLCH 9	1.04649	-0.24423	0.22171
SPLCH 10	1.51307	-0.32778	0.55807
CONTROL	-0.96007	-2.72036	-0.43245

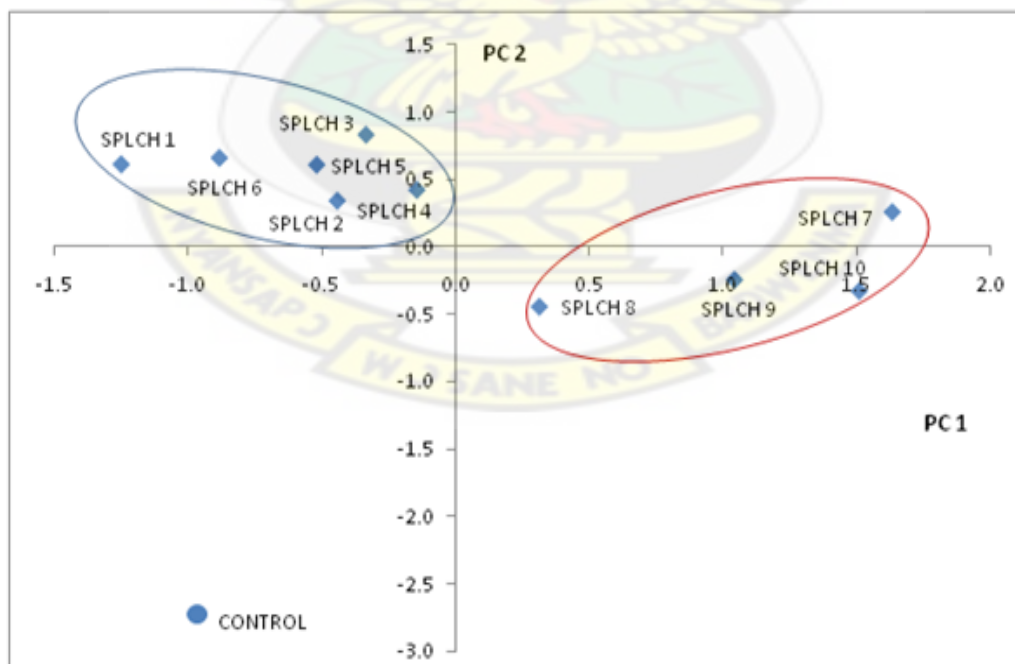


Fig.4.2: Plot of lichen principal component PC 1 versus principal component PC 2

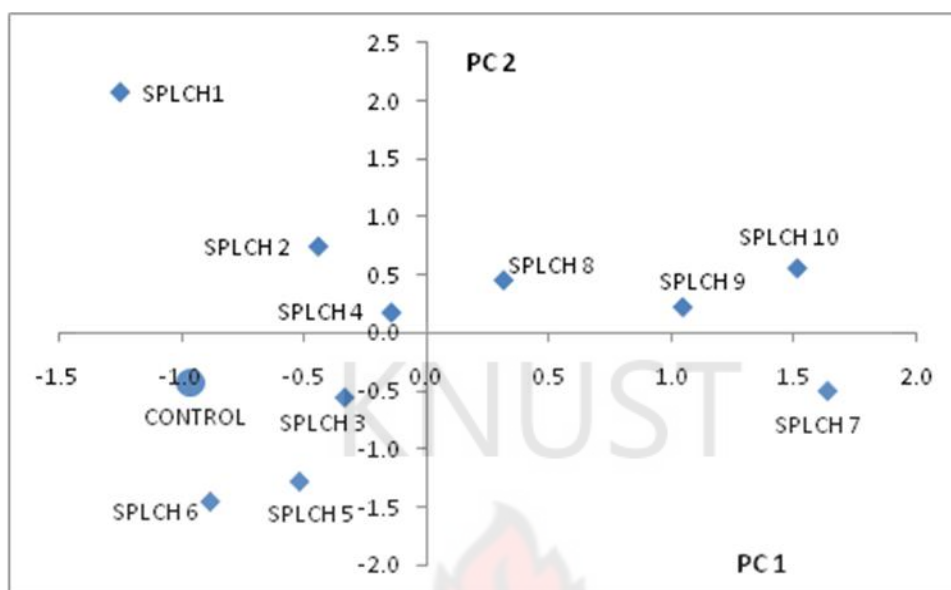


Fig. 4.3: Plot of lichen principal component PC 1 versus principal component PC 3

4.2.4 Cluster analysis (CA) of lichen data

(a) R-mode cluster analysis

The R-mode CA revealed 3 distinct groups or clusters. Fig. 4.4 presents a dendrogram showing different clusters of analyzed elements and their members. Cluster 1 contains Sb, V, Al and Cu. The elements Mn, Hg, Co and As are grouped in Cluster 2, whereas Cluster 3 contains Cd and Th. The groupings suggest that elements in a particular cluster are strongly correlated and may have probably originated from a common source.

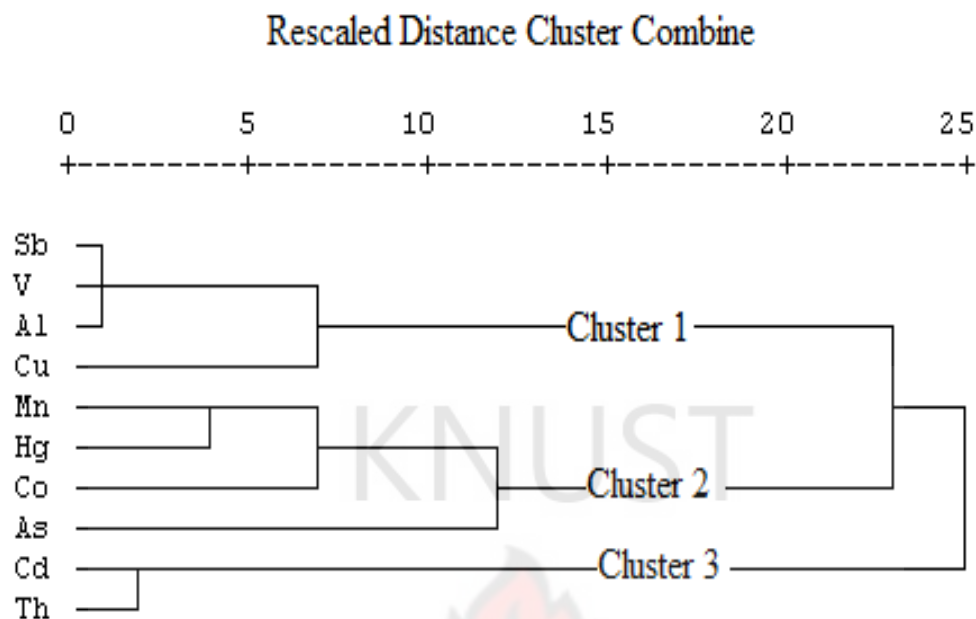


Fig. 4.4: Dendrogram of the measured elements in lichens

(b) Q-mode cluster analyses of lichen data

The cluster analysis (CA) results are presented in a dendrogram (Fig. 4.5), where all the 11 sampling sites, including the control site, are grouped into 3 statistically significant clusters. Group 1 consists of stations SPLCH5, SPLCH6, SPLCH1, SPLCH2, SPLCH3, SPLCH4 and SPLCH8. Group 2 consists of stations SPLCH9, SPLCH10 and SPLCH7. Group 3 consists of only the CONTROL site. The group classifications change with significance level because the sites in these groups have similar characteristic features that are affected by similar sources. Group 1 consists mainly of samples from Mile 6, Mile 7 and Mile 8 with the exception of SPLCH8, which was sampled from Teberebie. Group 1 corresponds to relatively moderate pollution (MP) sites. Group 2 consists of samples from only Teberebie and corresponds to a relatively high polluted (HP) site. Group 3 (CONTROL) also corresponds to relatively low polluted site (LP). This station is far from the Teberebie area, and is not influenced by any gold mining activity.

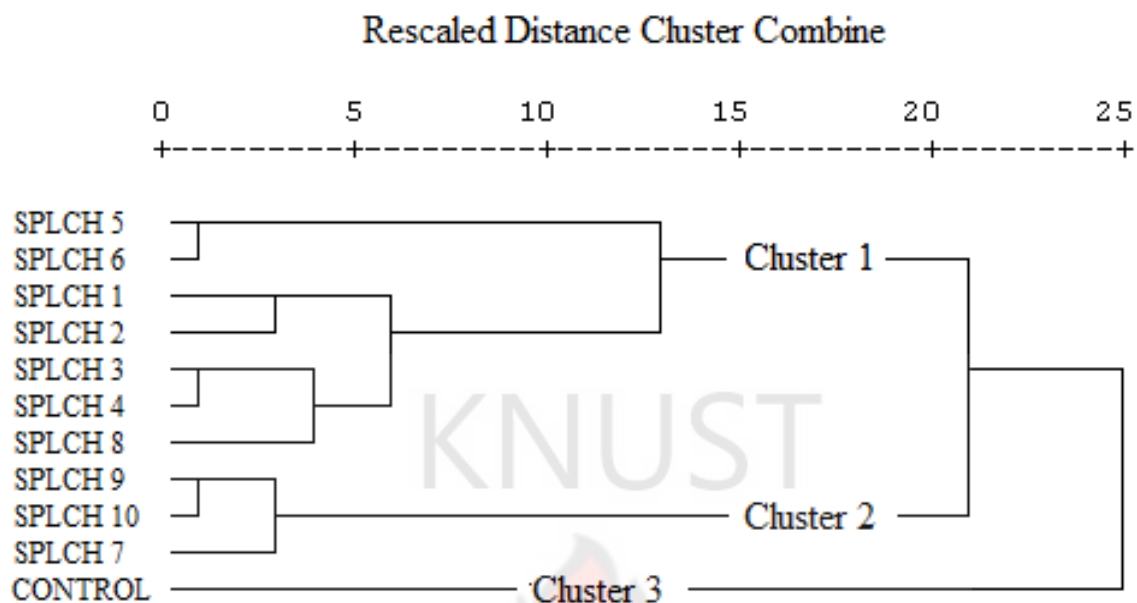


Fig. 4.5: Dendrogram showing clustering of analyzed lichen sample sites from the study area

4.3 SOIL

4.3.1 Concentrations of heavy metals in soil samples

The average concentrations of the examined elements in soil samples are presented in Table 4.7.

The average of INAA measurements of elements in soil samples from the communities are also given in Appendix 4. The distribution of the monitored elements in soils across the sampling points is shown by Appendix 3.

Table 4.7: Average concentration of heavy metals (ppm/dry weight) in soil samples

	Mile 6		Mile 7		Mile 8		Teberebie				CONTROL
	SPSL1	SPSL2	SPSL3	SPSL4	SPSL5	SPSL6	SPSL7	SPSL8	SPSL9	SPSL10	CONTRL
Sb	0.37	0.17	0.07	0.13	0.22	0.13	1.09	0.19	1.44	1.10	0.51
	<i>0.13</i>	<i>0.08</i>	<i>0.04</i>	<i>0.03</i>	<i>0.31</i>	<i>0.09</i>	<i>0.63</i>	<i>0.10</i>	<i>0.21</i>	<i>0.37</i>	<i>0.02</i>
Mn	15.500	7.52	22.10	59.20	45.84	36.39	1277	606	112	126	36.78
	<i>5.54</i>	<i>0.95</i>	<i>9.24</i>	<i>16.30</i>	<i>4.26</i>	<i>7.67</i>	<i>1579</i>	<i>618</i>	<i>55.8</i>	<i>12.4</i>	<i>3.61</i>
Cu	11.3	11.8	13.0	11.9	10.10	6.33	156	67.1	85.07	48.4	6.00
	<i>6.30</i>	<i>5.90</i>	<i>5.48</i>	<i>5.79</i>	<i>1.49</i>	<i>1.45</i>	<i>86.7</i>	<i>92.1</i>	<i>20.4</i>	<i>14.4</i>	<i>0.92</i>
V	14.60	16.57	2.88	2.49	1.71	0.62	182	7.03	55.00	60.20	3.78
	<i>6.67</i>	<i>3.10</i>	<i>1.46</i>	<i>0.45</i>	<i>0.35</i>	<i>0.32</i>	<i>324</i>	<i>3.07</i>	<i>17.5</i>	<i>6.53</i>	<i>0.07</i>
Al	4255	3081	2030	2259.00	2150	1884	16756	1913	994	6427	936
	<i>1974</i>	<i>1927</i>	<i>43.3</i>	<i>194</i>	<i>142</i>	<i>126</i>	<i>9733</i>	<i>717</i>	<i>993</i>	<i>12970</i>	<i>347</i>
Co	0.85	1.27	0.05	0.05	0.03	0.02	0.83	0.51	1.49	1.15	0.10
	<i>0.78</i>	<i>0.29</i>	<i>0.03</i>	<i>0.02</i>	<i>0.02</i>	<i>0.02</i>	<i>1.04</i>	<i>0.60</i>	<i>0.60</i>	<i>0.80</i>	<i>0.01</i>
Hg	0.01	0.01	0.01	0.01	ND	ND	0.02	0.01	0.01	0.01	3.20
	<i>0.01</i>	<i>0.01</i>	<i>0.001</i>	<i>0.001</i>	-	-	<i>0.02</i>	<i>0.01</i>	<i>0.01</i>	<i>0.01</i>	<i>0.10</i>
As	11.90	14.68	13.72	16.80	13.00	9.61	9.29	10.64	8.79	9.90	ND
	<i>6.23</i>	<i>9.24</i>	<i>9.79</i>	<i>7.16</i>	<i>7.57</i>	<i>5.28</i>	<i>5.52</i>	<i>2.74</i>	<i>3.19</i>	<i>4.02</i>	-
Cd	2.50	2.36	7.02	9.60	6.26	3.18	1.53	1.22	1.64	1.37	ND
	<i>1.39</i>	<i>1.30</i>	<i>4.37</i>	<i>1.95</i>	<i>1.45</i>	<i>0.93</i>	<i>1.06</i>	<i>1.43</i>	<i>1.78</i>	<i>0.49</i>	-
Th	0.30	0.16	0.08	0.06	0.01	0.01	0.08	0.14	0.03	0.09	0.10
	<i>0.39</i>	<i>0.08</i>	<i>0.03</i>	<i>0.01</i>	<i>0.01</i>	<i>0.01</i>	<i>0.06</i>	<i>0.16</i>	<i>0.01</i>	<i>0.09</i>	0.03

ND implies below detection limit

Concentrations in italics represent standard errors

The levels of Sb ranged between 0.07 and 1.44ppm. The relatively higher concentrations were recorded at sampling points SPSL7 (1.09ppm), SPSL9 (1.44ppm) and SPSL10 (1.10ppm) all at Teberebie. Mn concentrations in the soils were between 7.52 and 1277.3ppm. The highest levels were recorded from at the sampling points SPSL7, SPSL8, SPSL9 and SPSL10 all at Teberebie. The lowest Mn concentration (7.52ppm) was recorded at Mile 6 (SPSL2).

The Cu levels in soils are in the range of 6.33 to 156ppm. High levels (48.38-156ppm) were recorded at all the sampling points at Teberebie while Mile 8 sampling points registered the lowest values of 6.33–10.1ppm. Concentrations of V in the soils were between 0.62 and 182ppm.

The order of concentration levels of V with respect to communities were as follows: Teberebie > Mile 6 > Mile 7 > Mile 8.

Of all the analysed elements, Al recorded the highest concentrations in all the soils at the sampling points with the concentrations ranging between 994–16756ppm. The highest Al concentration occurred at Teberebie whereas Mile 8 recorded the least Al concentration. The Co levels in the soils ranged between 0.02–1.49ppm. The relatively high values were observed at SPSL2 (1.27ppm) at Mile 6 as well as SPSL9 (1.49ppm) and SPSL10 (1.15ppm) at Teberebie while SPSL6 (0.02ppm) at Mile 8 recorded the lowest value.

The Hg concentrations in the soils were the lowest compared with all the other elements, with all sampling points recording values less than 0.03ppm. Mile 8 soils had Hg values less than the detection limit of the INAA. About 70% of the sampling points had Hg concentrations of 0.01ppm. The sampling point 7 (SPSL7) of Teberebie had the highest level of 0.02ppm. The concentration of As in the soils is in the range of 8.79–16.80ppm. The highest and lowest concentrations were observed at Mile 7 and Teberebie, respectively.

The Cd levels in the soil samples ranged between 1.22 and 9.6ppm. The concentrations were almost evenly distributed across the sampling points with soil samples at Mile 7 having the highest levels. Teberebie had the lowest levels of the Cd in the soil samples. Th levels in the soil samples ranged between 0.01 to 0.30ppm. The Th levels in the soils were generally uniformly distributed in the samples.

4.3.2 Pollution Index Analyses of soil samples

The CFs and PLIs of each sampling point are shown in Table 4.8.

Table 4.8: Contamination Factors (CFs) and Pollution Load Indices (PLIs) of soil samples

		Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th	PLI
Mile 6	SPSL1	0.247	0.018	0.0004	0.1121	0.0532	0.045	0.025	0.916	8.333	0.025	0.069
	SPSL 2	0.113	0.009	0.0002	0.1275	0.0385	0.067	0.025	1.129	7.867	0.0133	0.053
Mile 7	SPSL 3	0.047	0.026	0.0006	0.0222	0.0254	0.003	0.025	1.055	23.4	0.0067	0.037
	SPSL 4	0.087	0.07	0.0015	0.0192	0.0282	0.003	0.025	1.290	32.0	0.005	0.048
Mile 8	SP SL5	0.147	0.054	0.0012	0.0132	0.0269	0.002	-	0.000	20.867	0.0008	0.05
	SPSL 6	0.087	0.043	0.001	0.0048	0.0236	0.001	-	0.739	10.60	0.0008	0.035
	SPSL7	0.727	1.503	0.0334	1.400	0.2094	0.044	0.050	0.715	5.10	0.0067	0.237
	SPSL8	0.127	0.713	0.0158	0.0541	0.0239	0.027	0.025	0.818	4.067	0.0117	0.09
Teberebie	SPSL9	0.960	0.132	0.0029	0.4227	0.0124	0.078	0.025	0.676	5.467	0.0025	0.09
	SPSL10	0.733	0.148	0.0033	0.4631	0.0803	0.061	0.025	0.762	4.567	0.0075	0.118
	CONTROL	0.340	0.043	0.001	0.0291	0.0117	0.005	-	0.000	-	0.0083	0.04

Almost all the sampling points have Contamination Factors less than unity for Sb, Mn, Cu, V, Al, Co, Hg and Th (Table 4.8). Exceptions include sampling point 7 (SPSL7) of Teberebie, where CFs of 1.50 and 1.40 were recorded for Mn and V, respectively. All the sampling points record CF values more than unity for Cd. For As, sampling points, SPSL 2, SPSL 3 and SPSL 4 show CF values of 1.13, 1.06 and 1.29, respectively, whereas the rest of the sampling points have CF values less than unity. The sampling points show variations in the PLI values. However, all the sampling points have PLI values less than 1.0. The community with the highest PLI value of 0.12 was Teberebie. This was followed by Mile 6 with PLI value of 0.06 and Mile 7 and 8 soil samples with the same value of 0.04.

The results for the individual elemental geoaccumulation (Igeo) values for each sampling point are presented in Table 4.10. The soils were classified using the table of seven classes of

Geoaccumulation index values used by Grzebisz *et al.* (2002), Lokeshwani and Chandrappa *et al.* (2007) and Yaqin *et al.* (2008) [Table 4.9].

Table 4.9: The seven classes of Geoaccumulation index values

I_{geo} Value	I_{geo} Class	Intensity of pollution
<0	1	Practically unpolluted
>0-1	2	Unpolluted to moderately polluted
>1-2	3	Moderately polluted
>2-3	4	Moderately to strongly polluted
>3-4	5	Strongly polluted
>4-5	6	Strongly to very strongly polluted
>5	7	Very strongly polluted

Table 4.10. Geoaccumulation Index (I_{geo}) of soil samples

		Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th
Mile 6	SPSL1	2.604	-6.36	-2.575	-3.742	-4.818	-5.07	-5.91	-0.71	2.4739	-5.907
	SPSL 2	-3.76	-7.41	-2.515	-3.557	-5.284	-4.49	-5.91	-0.41	2.3908	-6.814
Mile 7	SPSL 3	-5.01	-5.85	-2.382	-6.081	-5.886	-9.16	-5.91	-0.507	3.9635	-7.814
	SPSL 4	-4.11	-4.43	-2.503	-6.291	-5.731	-9.55	-5.91	-0.215	4.415	-8.229
Mile 8	SPSL5	-3.54	-4.8	-2.741	-6.833	-5.803	-9.89	-	-0.585	3.7982	-10.81
	SPSL 6	-4.11	-5.13	-3.415	-8.297	-5.993	-10.5	-	-1.021	2.821	-10.81
	SPSL7	-1.05	0.003	1.209	-0.100	-2.84	-5.1	-4.91	-1.07	1.7655	-7.814
	SPSL8	-3.57	-1.07	-0.01	-4.794	-5.971	-5.8	-5.91	-0.874	1.4389	-7.006
Teberebie	SPSL9	-0.64	-3.51	0.3338	-1.827	-6.915	-4.26	-5.91	-1.15	1.8657	-9.229
	SPSL10	-1.03	-3.34	-0.48	-1.696	-4.223	-4.63	-5.9	-0.978	1.6062	-7.644
	CONTROL	-2.14	-5.12	-3.492	-5.689	-7.003	-8.17	-	-7.607	-	-7.490

The I_{geo} values (Table 4.10) for Sb, V, Al, Co, Hg, As and Th were less than 1.0 for all the sampling points (except for SPSL1, where the I_{geo} value of Sb was 2.60), indicating practically unpolluted soils. The I_{geo} values for Cd were >1.0 for all the sampling points. SPSL3 and SPSL4 of Mile 7 recorded the highest I_{geo} values of Cd of 3.96 and 4.42, respectively, suggesting strongly polluted soils. The Mile 6 soil samples (SPSL1 and SPSL2) recorded I_{geo}

values of Cd between 2.39 and 2.47, indicating moderately to strongly polluted soils. Teberebie sampling points (SPSL7, SPSL8, SPSL9 and SPSL10) registered Igeo values for Cd in the range of 1.44–1.87, indicating moderately polluted soils. The sampling points, SPSL5 and SPSL6 of Mile 8 had Igeo values for Cd of 2.82 and 3.80, respectively, representing moderately to strongly polluted soils.

The results of the Enrichment Factor analysis for soil samples are presented in Table 4.11.

Table 4.11: Sampling points and their Enrichment Factors (EFs)

		Sb	Mn	Cu	V	Co	Hg	As	Cd	Th
Mile 6	SPSL1	4.637	0.34	4.73	2.11	0.84	0.47	17.2	0.002	0.47
	SPSL 2	2.943	0.23	6.81	3.31	1.74	0.649	29.3	0.0026	0.35
Mile 7	SPSL 3	1.84	1.02	11.3	0.87	0.1	0.986	41.6	0.0115	0.26
	SPSL 4	3.069	2.47	9.37	0.68	0.09	0.885	45.8	0.0142	0.18
Mile 8	SP SL5	5.459	2.01	8.35	0.49	0.06	0	37.2	0.0097	0.03
	SPSL 6	3.68	1.82	5.97	0.2	0.04	0	31.4	0.0056	0.04
	SPSL7	3.469	7.17	16.6	6.68	0.21	0.239	3.41	0.0003	0.03
	SPSL8	5.297	29.8	62.3	2.26	1.12	1.046	34.2	0.0021	0.49
Teberebie	SPSL9	77.23	10.6	152	34	6.31	2.011	54.4	0.0055	0.2
	SPSL10	9.128	1.85	13.4	5.76	0.75	0.311	9.48	0.0007	0.09

EF less than 3 is depleted to minimal enriched

EF value 3-5 is moderately enriched

EF value 5-10 is significantly enriched.

All the soils analysed are significantly enriched with Cu and As as shown by the Enrichment Factor (EF) which are greater than 5 with the exception of sampling point 1 (SPSL1) with an EF of 4.73. The soil samples from SPSL2 and SPSL3 recorded EF values of 2.94 and 1.84 respectively for Sb, indicating depletion to minimal enrichments. The rest of the soil samples are moderately or significantly enriched with Sb. The EF values for Mn for sampling points 1, 2, 3, 4, 5, 6 and 10 were between 0.23 to 2.46 indicating depletion to minimal enrichment soils, whereas that of sampling points 7, 8 and 9 were >5 indicating significant enrichment. The sampling point 7 and 1 recorded EF value of 3.41 and 4.73 respectively for As representing

moderately enriched soil and all the other sampling points recorded EFs >5, indicating that the soils are significantly enriched with As. The EF values for Hg, Cd, and Th were less than 3 indicating depletion to minimal enrichment for all the sampling points. All the sampling points were significantly enriched with Cu with EF values >5. Apart from sampling point 9, which recorded EF value of 6.3 for Co, all the rest of the sampling points had values less than 3 indicating depleted to minimal enrichments.

4.3.3 Interrelations of heavy metals in soils

(a) Associations of heavy metals in soil samples

The Spearman's correlation matrix for elemental levels in the soil samples is presented in Table 4.12. There were significant correlations at the 0.01 level between the elements Sb, Mn, Cu, V and Co. There existed some positive correlation at the 0.05 level between Hg, Cu and Al. Cadmium (Cd) was negatively correlated with Sb, Mn, Cu, V, Co and Hg but positively correlated at the 0.01 level with As. Thorium (Th) was positively correlated with V, Al and Co at the 0.01 level.

Table 4.12: Correlation matrix for elements in the soils of study area

	Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th
Sb	1									
Mn	.417**	1								
Cu	.701**	.645**	1							
V	.806**	.311*	.766**	1						
Al	0.086	0.012	0.095	0.15	1					
Co	.747**	0.174	.614**	.865**	0.175	1				
Hg	0.252	0.261	.281*	0.14	.348*	0.058	1			
As	-0.054	-0.098	0.115	0.01	0.13	0.203	-0.074	1		
Cd	-.342**	-.279*	-.347**	-.409**	0.183	-.239*	-0.148	.517**	1	
Th	0.225	-0.14	0.28	0.469**	0.382**	0.543**	0.016	0.16	-0.095	1

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level

(b) R-mode principal component analysis of soil data

The results of the R-mode PCA is presented in Table 4.13 with significant factor loadings in bold faced. Three principal components were obtained with Eigenvalues > 1 , explaining 86.4% of the total variance in soil dataset. The first PC, accounting for 38.125% of the total variance was correlated with Sb, Cu, Co, V, As and Cd. However, As and Cd were negatively correlated. The second PC, explaining 29.915% of the total variance was correlated primarily with V, Co, Hg and Th. The third PC, accounting for 18.398% of the total variance, was weighted on Mn, Cu and Al.

Table 4.13: Rotated component matrix of 3 factor model explaining 86.4% of the total variance for soil

	PC 1	PC 2	PC 3
Sb	0.831	0.194	0.291
Mn	0.475	-0.099	0.791
Cu	0.700	0.270	0.572
V	0.638	0.610	0.377
Al	0.063	0.390	0.711
Co	0.656	0.741	0.005
Hg	0.153	0.862	0.323
As	-0.892	0.240	-0.196
Cd	-0.862	-0.305	-0.111
Th	-0.039	0.950	0.033
Eigenvalue	3.812	2.992	1.84
% of total variance	38.125	29.915	18.398
Cumulative % of variance	38.125	68.04	86.438

(c) Q-Mode principal component analysis of soil data

Using Q-mode PCA, the sampling sites were classified according to the factor loading levels of elements present in the three PCs given in Table 4.13. The factor scores for the three principal components identified in Table 4.13 are given by Table 4.14.

Table 4.14: Varimax rotation factor scores for the three factor model for the analyzed soil samples

	PC 1	PC 2	PC 3
SPSL 1	-0.102	1.128	-0.752
SPSL 2	-0.342	1.260	-1.157
SPSL 3	-1.231	0.167	-0.104
SPSL 4	-1.592	0.106	0.488
SPSL 5	-0.499	-1.510	-0.016
SPSL 6	0.053	-1.860	-0.574
SPSL 7	0.569	0.343	2.354
SPSL 8	0.474	0.135	0.260
SPSL 9	1.813	-0.200	-0.875
SPSL 10	0.857	0.431	0.375

From PC1 of Table 4.13, the elements Sb, Cu, Co, V, As and Cd are highly concentrated at SPSL9 and SPSL10 with factor scores of 1.813 and 0.857, respectively (Table 4.14). PC2 represents strong correlations and distribution patterns for V, Co, Hg and Th at sampling points SPSL1 and SPSL2. PC3 shows strong correlation for the elements Mn, Cu and Al at sampling point SPSL7. Fig. 4.6 presents a plot of the factor scores of sampling points on a bidimensional plane defined by PC1 and PC2. This plot puts the 10 sampling points into 2 dimensions explaining 68.04% of the total variance. From the diagram, 3 distinct groups with regards to the examined elements emerge. Group 1 consists of samples from Teberebie (SPSL7, SPSL8, SPSL9 and SPSL10). Group 2 is the combination of samples from Mile 6 (SPSL1 and SPSL2)

and Mile 7 (SPSL3 and SPSL4) whereas Group 3 contains samples from Mile 8 (SPSL5 and SPSL6).

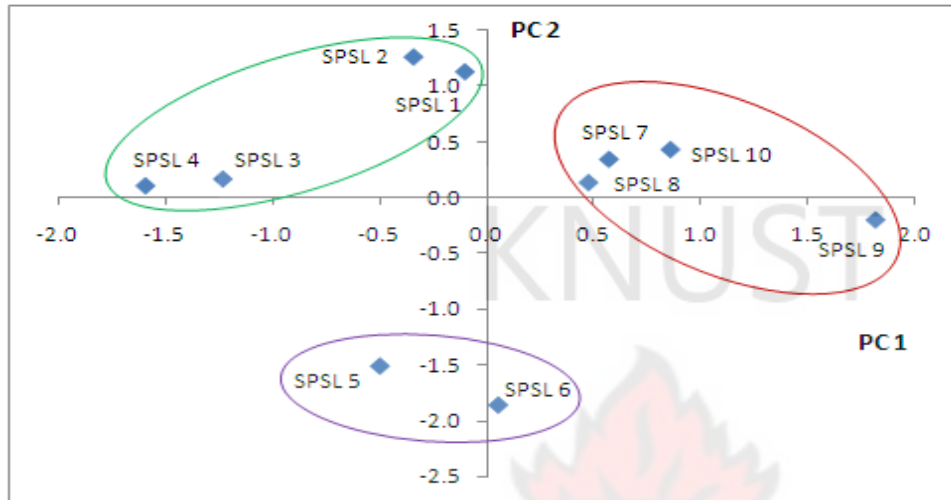


Fig. 4.6: Plot of soil principal component PC 1 versus principal component PC 2.

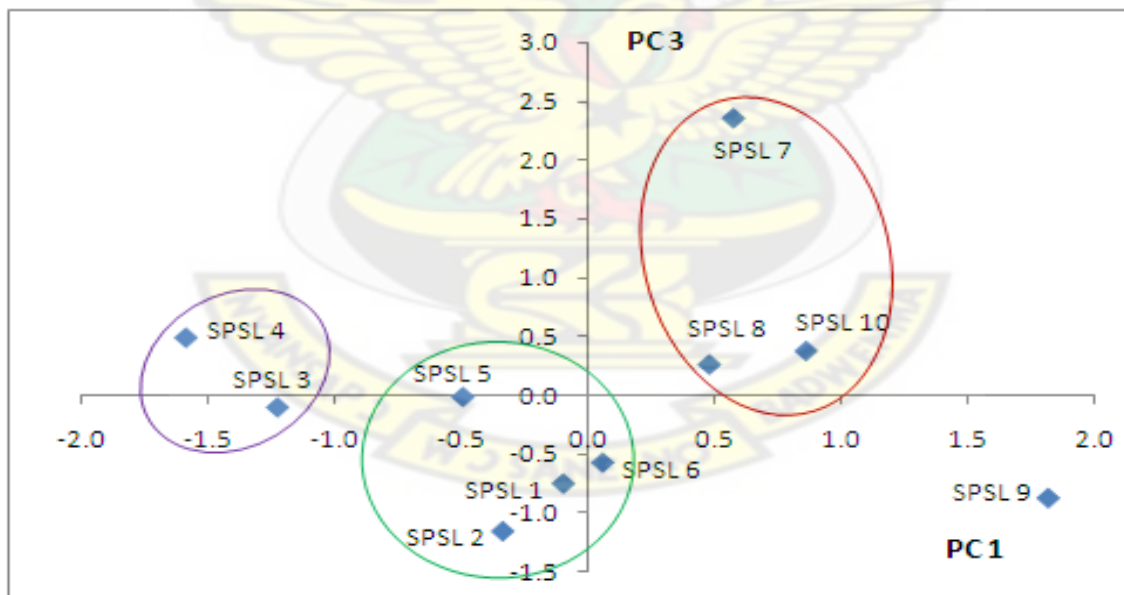


Fig. 4.7. Plot of soil principal component PC 1 versus principal component PC 3.

A plot of factor scores of PC1 versus PC3 produces 3 unique groups of soil comprising Teberbie group, Mile 7 and Mile 8 group, and Mile 6 group (Fig. 4.7). The results from the Fig.

4.6 and 4.7 show that at least the soils from Teberebie may be distinguished from those of Mile 6, Mile 7 and Mile 8 with regards to the heavy metals analysed.

(d) Cluster analysis of soil data

The R-mode CA revealed two distinctive groups or clusters (Fig. 4.8). Cluster 1 contains V, Co, Sb, Al, Mn, Cu, Hg and Th, whereas Cluster 2 contains As and Cd. The R-mode CA results suggest V, Co, Sb, Al, Mn, Cu, Hg and Th move together and may have a common source. Similarly, As and Cd probably originated from a common source.

Cluster analysis in Q-mode is represented by a dendrogram in Fig. 4.9. According to the dendrogram the sampling points can be grouped into two clusters. Cluster 1 contains SPSL1, SPSL2, SPSL3, SPSL4, SPSL5 and SPSL6, whereas Cluster 2 contains SPSL7, SPSL8, SPSL9 and SPSL10. Thus, the Q-mode CA shows that the soils of Teberebie (SPSL7, SPSL8, SPSL9 and SPSL10) are quite distinct from the soils of Mile 6, Mile 7 and Mile 8 (SPSL1, SPSL2, SPSL3, SPSL4, SPSL5 and SPSL6).

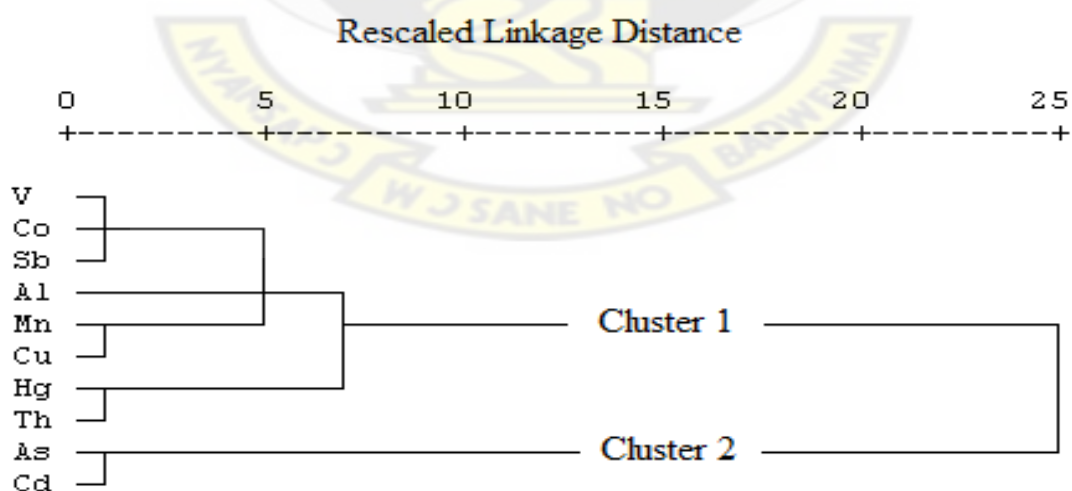


Fig. 4.8: Dendrogram of the measured elements in soils

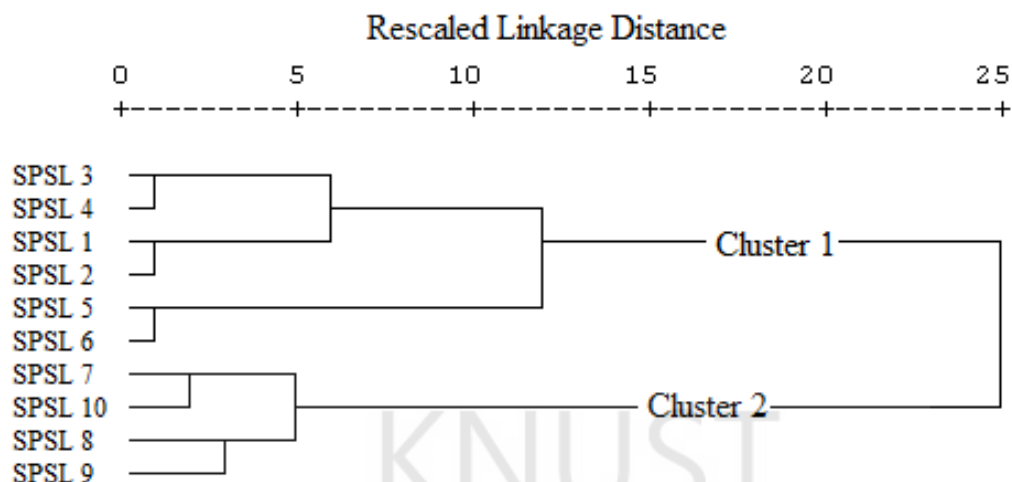


Fig.4.9: Dendrogram showing clustering of analyzed soil sample points from the study area

4.4 LICHEN AND SOIL RELATIONSHIPS

4.4.1 Variation of heavy metals levels in lichen and soil

In general the Sb, Mn, and Hg levels in soils were lower than those found in lichens. However, the Cu, Cd and Al concentrations in soils were higher than those found in lichens. Fig. 4.10 to Fig. 4.19 present a pictorial impression of the concentrations of the 10 elements in soils and lichens at the various sampling points.

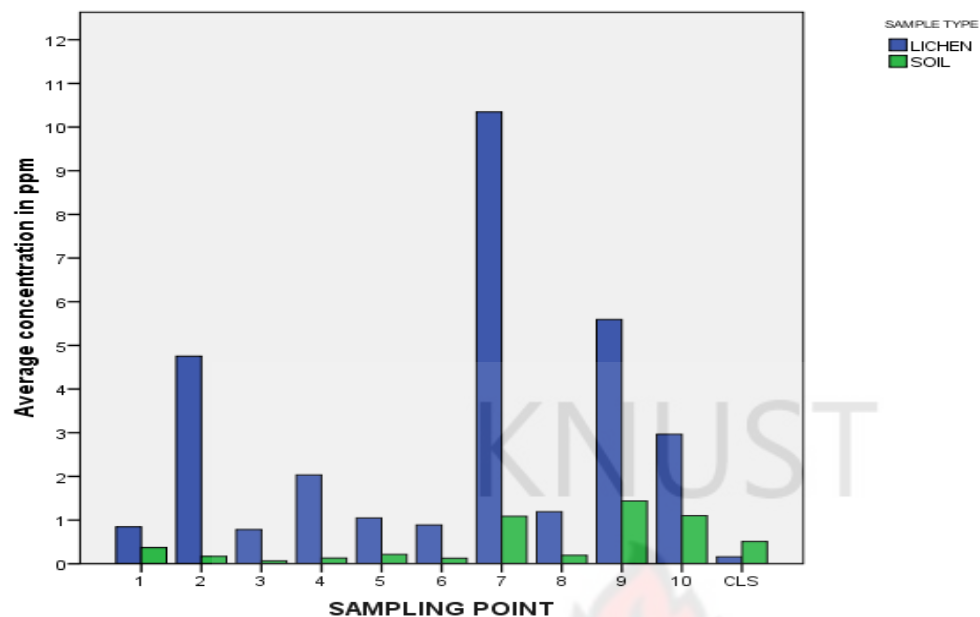


Fig.4.10: Comparison of Sb concentration in lichen and soil samples.

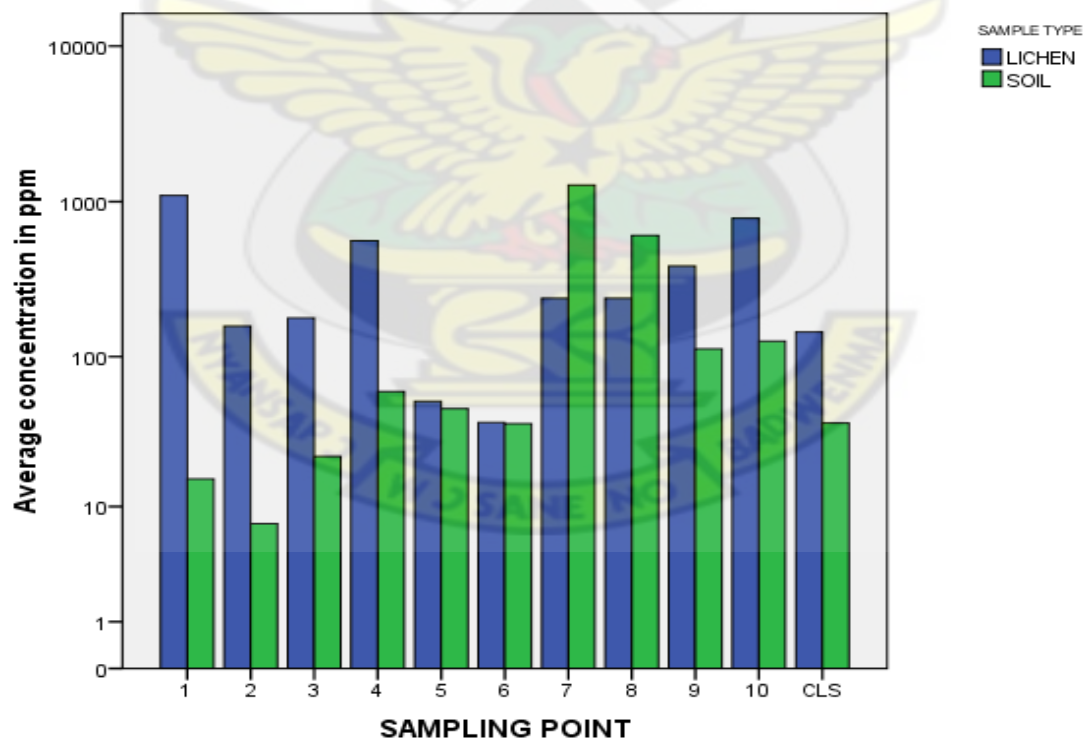


Fig.4.11: Comparison of Mn concentration in lichen and soil samples

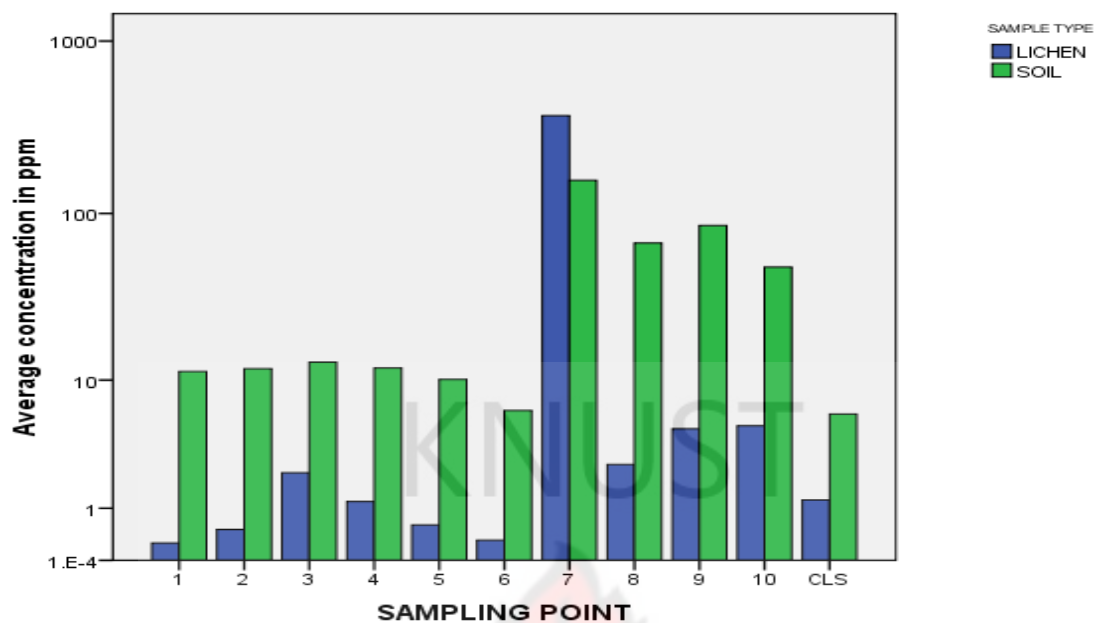


Fig.4.12: Comparison of Cu concentration in lichen and soil samples

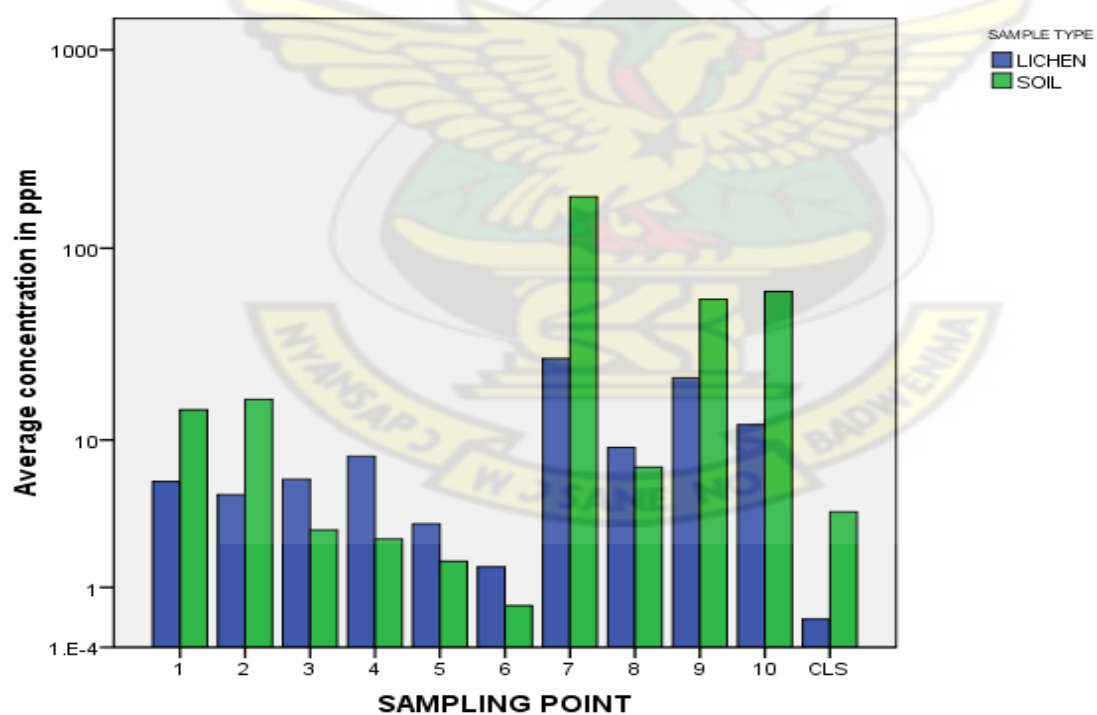


Fig.4.13: Comparison of V concentration in lichen and soil samples

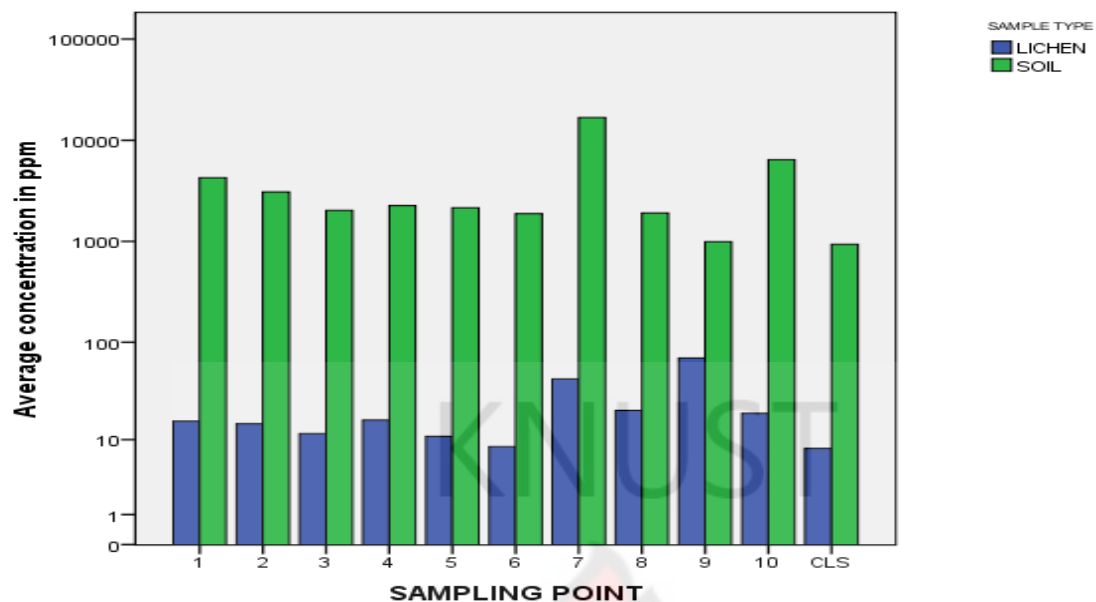


Fig.4.14: Comparison of Al concentration in lichen and soil samples

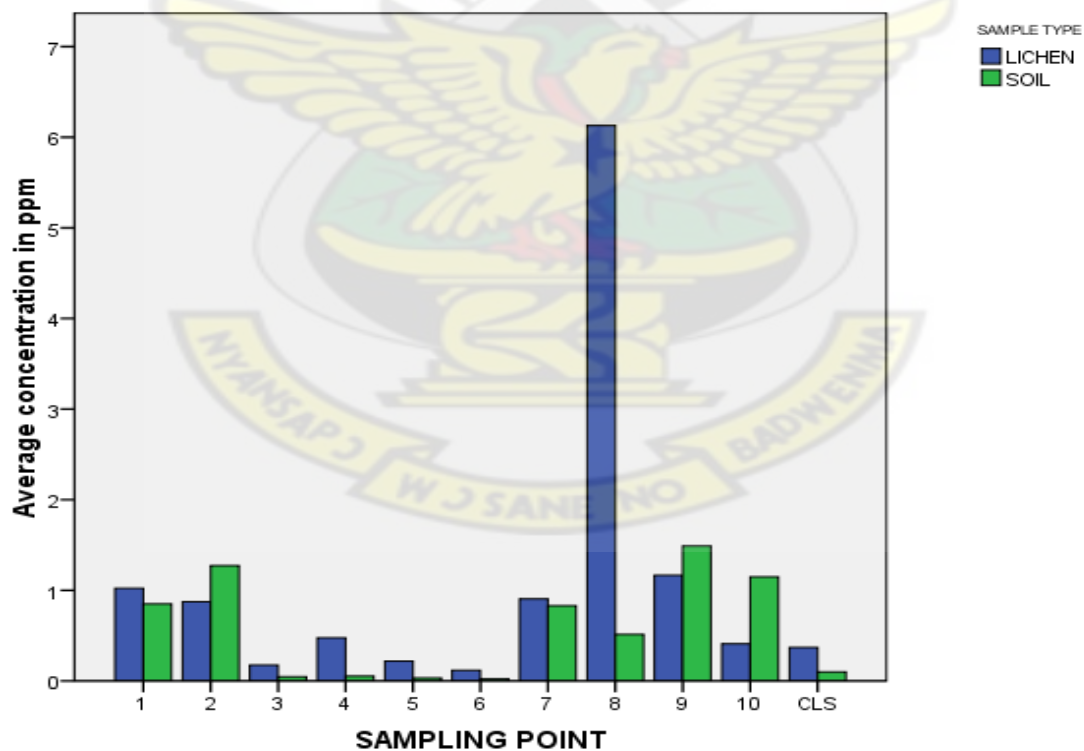


Fig.4.15: Comparison of Co concentration in lichen and soil samples

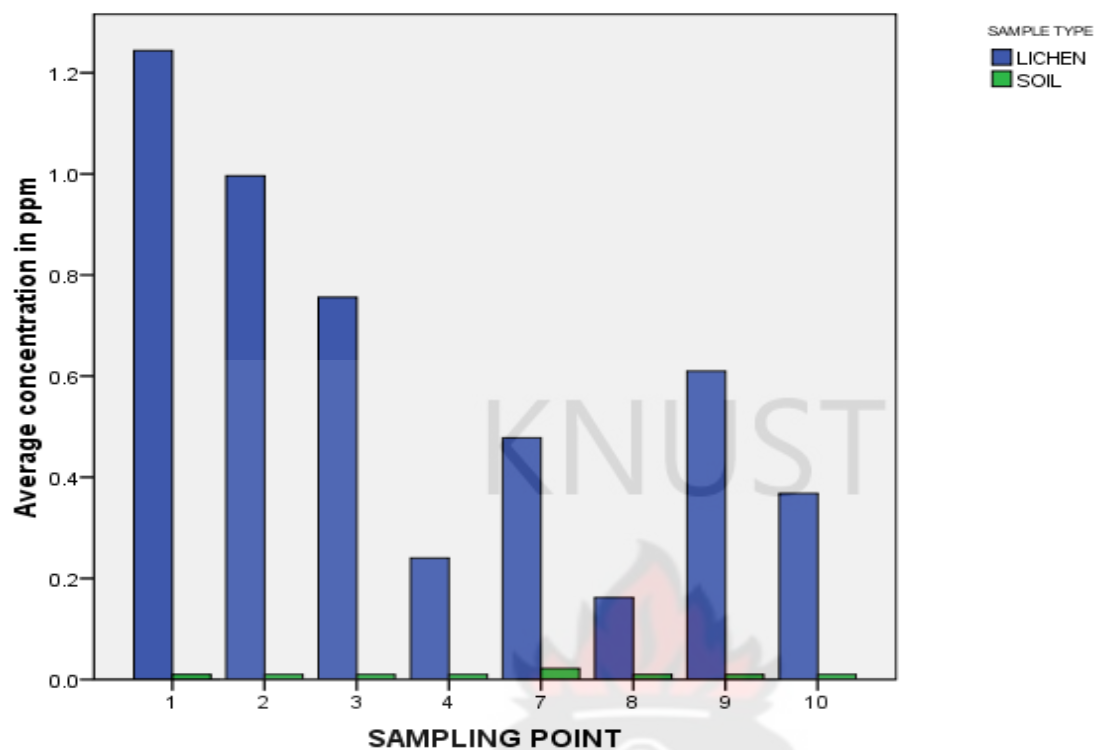


Fig.4.16: Comparison of Hg concentration in lichen and soil samples.

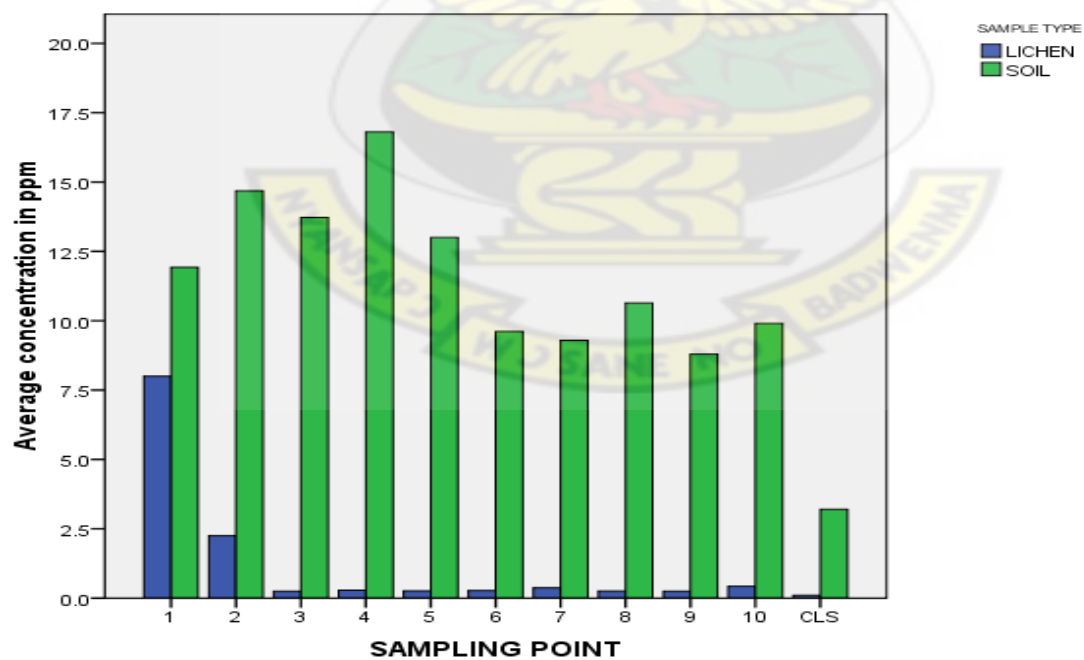


Fig.4.17. Comparison of As concentration in lichen and soil samples

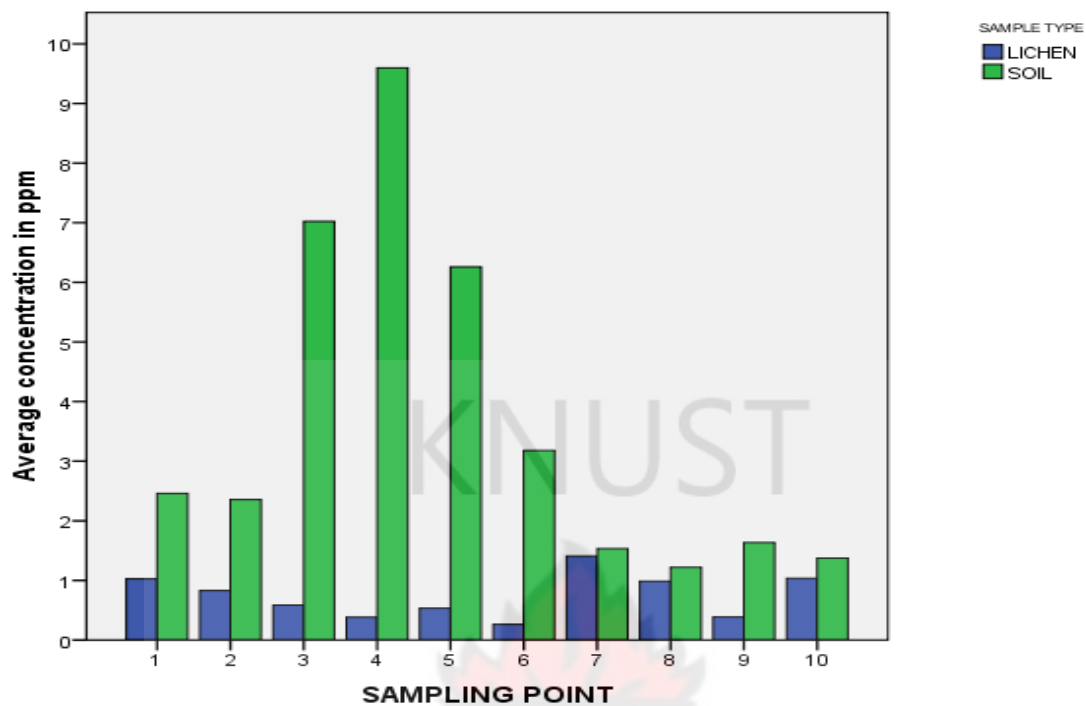


Fig.4.18: Comparison of Cd concentration in lichen and soil samples

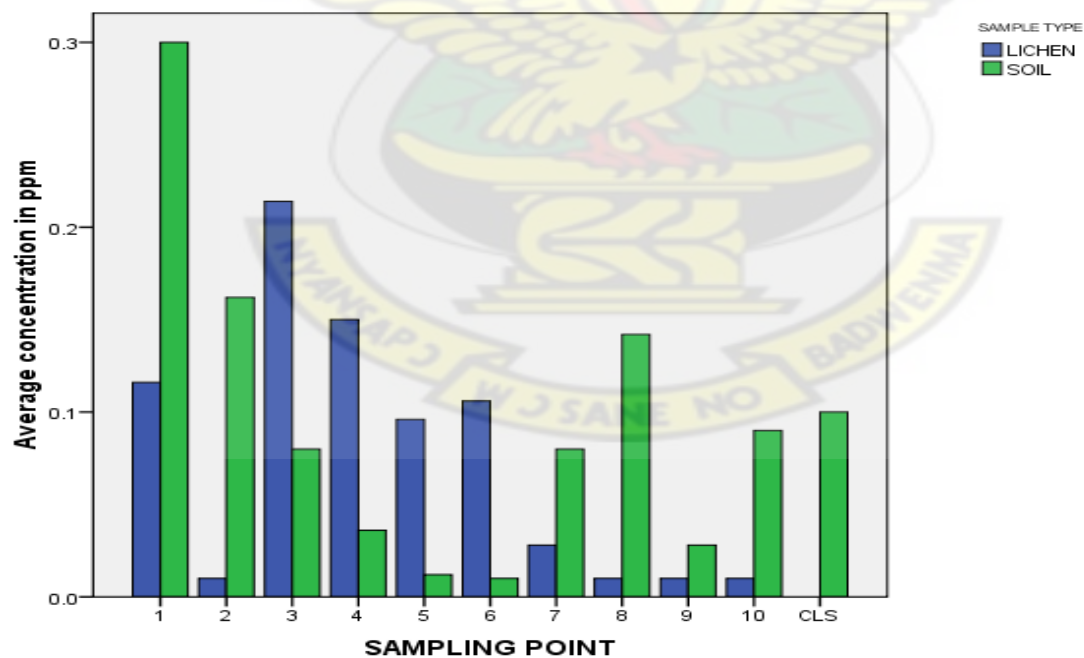


Fig.4.19: Comparison of Th concentration in lichen and soil samples

4.4.2 Lichen samples collection and soil contamination analysis

Table 4.15 shows the mean Enrichment Factors (EFs) for the monitored elements based on element concentrations in lichens normalized to the Al content of the soil samples and estimated background concentrations (ECs).

As a rule, the closer the EFs to unity, the greater the derivation of the element in question from the soil (Bargagli, 1995; Loppi *et al.*, 1999; Nyarko *et al.*, 2006). The EF value of 1 – 5 suggests that the elements in lichen were essentially due to soil contamination of the soils, whilst value between 10 and 20 indicate that a substantial amount was of atmospheric origin. The EF value above 30 clearly confirms that the element has the tendency to behave as atmophile element subject to long-range atmospheric transport (Loppi *et al.*, 1999)

Table 4.15. Enrichment Factors calculated for all elements using Al as a reference element, and estimated background (EC) concentrations (ppm) of elements, assuming 8 ppm of Al as baseline for the non-particulate fraction and ascribing the excess of Al to trapped soil particles.

		SPLCH1	SPLCH2	SPLCH3	SPLCH4	SPLCH5	SPLCH6	SPLCH7	SPLCH8	SPLCH9	SPLCH10
Sb	EF	622	5824	1948	2178	944	1539	3719	588	55.5	1058
	EC	0.849	4.75	0.780	2.03	1.05	0.890	10.3	1.19	5.50	13.3
Mn	EF	19158	4366	1406	1319	221	229	73.1	37.0	49.2	333
	EC	1097	157	178	560	51.1	37.1	236	235	379	480
Cu	EF	6.22	9.00	29.8	13.9	11.7	11.0	928	3.62	0.798	34.8
	EC	0.239	0.484	2.19	1.15	0.587	0.309	369	2.15	-0.515	18.8
V	EF	108	60.9	363	454	370	556	58.6	121	5.61	57.4
	EC	5.76	4.80	5.97	8.09	3.20	1.53	26.9	9.03	18.2	39.0
Co	EF	325	143	594	1339	1450	1349	425	1129	11.2	299
	EC	1.02	0.867	0.170	0.480	0.220	0.120	0.898	6.13	1.08	3.93
Hg	EF	33587	20845	13284	3347	-	-	9400	1503	872	7679
	EC	1.24	1.00	0.760	0.240	0.001	0.001	0.480	0.160	0.609	0.880
As	EF	182	31.9	3.18	2.32	3.95	6.32	16.4	2.21	0.41	3.44
	EC	7.98	2.22	0.226	0.219	0.243	0.268	0.371	0.181	-0.294	0.289
Cd	EF	111	73.3	14.4	5.52	16.7	18.4	361	76.2	3.40	35.0
	EC	1.02	0.825	0.568	0.345	0.522	0.259	1.41	0.982	0.288	0.536
Th	EF	108	13.0	459	349	1977	2473	147	6.71	4.77	9.70
	EC	0.119	0.010	0.210	0.150	0.100	0.110	0.030	0.009	0.008	0.009

4.5 STREAMS WATER AND SEDIMENTS

4.5.1 Rivers

(a) Concentrations of heavy metals in riverine water and sediment samples

The mean concentrations of the 10 examined heavy metals (Sb, Mn, Cu, V, Al, Co, Hg, As, Cd and Th) in Angonabeng, Bediabewu and Kakum river water and sediment samples are reported in Table 4.17.

For the water samples, Angonabeng river recorded the highest average Sb concentration of 41.44ppm while Bediabewu river registered 10.7ppm. The Sb, Cu, Hg, Cd and Th concentrations in the reference river (Kakum) water samples were all below the detection limits. However, Bediabewu river sediment recorded the highest deposits of Sb (308.9ppm). The average Sb concentration in Angonabeng river sediment was 38.9ppm. The reference river sediment recorded Sb concentration of 3.23ppm.

Table 4.17: Average values (ppm) of heavy metals in river water and sediment samples

	Angonabeng River		Bediabewu River		Kakum River	
	Sediment	Water	Sediment	Water	Sediment	Water
Sb	38.9 ± 29.1	41.4 ± 13.9	309±509	10.7 ± 10.4	3.23 ± 4.79	ND
Mn	36468 ± 47165	17.8 ± 27.2	365±407	8.04 ± 7.56	777 ± 1361	0.760 ± 0.710
Cu	13.0 ± 4.40	3.66 ± 1.11	20.1±17.3	5.59 ± 2.58	3.21 ± 3.93	ND
V	133 ± 35.6	0.37 0± 0.240	417±637	0.378 ± 0.420	30.6 ± 19.0	0.120 ± 0.020
Al	86423 ± 126042	13.8 ± 9.39	172274±180616	14.6 ± 1.45	15836 ± 23802	1.450 ± 0.760
Co	2.09 ± 0.116	4.09 ± 3.36	20.0±17.0	2.30 ± 1.37	5.17 ± 3.68	0.064 ± 0.020
Hg	0.212 ± 0.149	1.48 ± 0.256	0.054±0.038	0.522 ± 0.51	ND	ND
As	5.41 ± 5.95	12.2 ± 7.02	13.4±10.4	18.4 ± 2.54	1.31 ± 0.732	0.010 ± 0.010
Cd	0.658 ± 0.584	1.11 ± 0.361	0.312±0.263	1.11 ± 0.080	ND	ND
Th	1.64 ± 0.783	0.286 ± 0.18	15.72±13.2	0.198 ± 0.145	12.9±4.41	ND

ND implies not detected

The average Mn concentrations in the water samples of Angonabeng, Bediabewu and Kakum rivers were 17.8ppm, 8.04ppm and 0.76ppm, respectively. Angonabeng river recorded the highest Mn concentration of 36468ppm in sediments samples. Mn concentrations of 365 and 777ppm were reported for Bediabewu and Kakum river sediment samples respectively. Bediabewu river registered the highest Cu levels in both water and sediment samples. Average Cu levels in water samples of 5.6ppm and 3.7ppm were reported for Bediabewu and Angonabeng rivers respectively. Bediabewu and Angonabeng recorded V levels 0.37 and 0.38ppm respectively in water samples whereas 0.12ppm was reported for Kakum river water samples. Bediabewu recorded the highest (417ppm) level of V in sediment samples. Angonabeng and Kakum had average V concentrations of 133.24ppm and 30.62ppm respectively.

The average Al concentration (86423ppm) in sediment samples of Angonabeng river was the highest and Bediabewu river was next with 172274ppm whereas Kakum river recorded the lowest of 15836ppm. Average Al levels in water samples of Bediabewu river was highest (14.6ppm), followed by Angonabeng river (13.78ppm) and Kakum river recording the lowest level of 1.45ppm.

The average Co concentration in water samples of Angonabeng river (4.1ppm) was almost twice of that recorded for Bediabewu river (2.3ppm) water samples. Kakum river recorded the lowest Co level in water (0.064ppm). However, Bediabewu river sediment samples registered the highest (20.02ppm) deposits of Co. The Co concentrations in Angonabeng and Kakum river sediments were 2.1ppm and 5.17 ppm, respectively.

The Hg and Cd levels in Kakum river sediments were less than the detection limits. However, Angonabeng river water had the highest amount of Hg of 1.484ppm while Bediabewu recorded average Hg level of 0.522ppm. The average Hg deposits in the sediment samples of Bediabewu river was 0.054ppm and that of Angonabeng river was 0.212ppm. Bediabewu river had the highest (18.4ppm) amount of As in the water samples followed by Angonabeng river (12.2ppm) with Kakum river having the least value of 0.01ppm. Generally, the level of As in sediment samples was lower than that of the water samples with Bediabewu river recording 13.4ppm whereas Angonabeng river had 5.41ppm and Kakum with 1.31. The average Cd concentrations in Angonabeng and Bediabewu river water samples were almost the same for the two rivers (1.114 and 1.112ppm respectively). Average Cd concentrations in sediment samples were relatively lower than that found in water. Angonabeng river had average Cd level (0.658ppm) in sediments which was almost twice that of Bediabewu river (0.312ppm).

The average Th concentration in Bediabewu river sediment was the highest (15.72ppm) followed by Kakum river (12.91ppm) with Angonabeng river having the least value of 1.636ppm. However, the Angonabeng river water registered the highest (0.286ppm) level of Th in water samples while Bediabewu river water recorded an average concentration of 0.198ppm.

In general, the ranking of elements in river water samples in terms of concentrations was as follows: Sb>Al>Mn>As>Cu>Co>Cd>Hg>Th>V. The ranking of elements in river sediments with respect to concentrations in Angonabeng and Bediabewu river samples was as follows: Al>Mn>V>Sb>Cu>Co>As>Th>Cd>Hg. Generally, the concentrations of the elements in the river sediments were higher than that of the water samples.

(a) Relationships of the elements in riverine water and sediment samples

The correlation matrix (Table 4.18) of the elements in the two rivers of the study area demonstrates good inter-relationships between Sb, Mn, Cu, V, Al, Co, Hg, As, Cd and Th.

Table 4.18: Correlation matrix of levels of heavy metals in riverine sediment and water samples

A	Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th
Sb	1									
Mn	0.333	1								
Cu	0.806**	0.442	1							
V	0.891**	0.539	0.830**	1						
Al	0.693*	0.036	0.34	0.565*	1					
Co	0.552*	-0.261	0.309	0.503	0.790**	1				
Hg	0.049	0.571*	0.547	0.31	-0.34	-0.401	1			
As	0.842**	0.03	.697*	.806**	0.717**	0.818**	0.012	1		
Cd	0.371	0.705*	0.529	0.620*	0.308	0.067	0.668*	0.353	1	
Th	0.855**	-0.02	0.54	0.758**	0.809**	0.879**	-0.31	0.915**	0.14	1
B										
Sb	1									
Mn	0.588*	1								
Cu	0.018	.648*	1							
V	0.758**	.867**	0.503	1						
Al	0.321	.770**	0.37	0.479	1					
Co	0.733**	.818**	0.43	.842**	0.43	1				
Hg	0.863**	0.274	-0.07	0.547	-0.073	0.426	1			
As	0.03	.745**	.806**	0.515	.782**	0.358	0.237	1		
Cd	0.492	.748**	0.267	0.608*	0.827**	0.669*	0.082	0.620*	1	
Th	.774**	.927**	0.4	0.902**	0.756**	0.787**	0.456	0.591*	0.755**	1

* Correlation is significant at the 0.05 level

** Correlation is significant at the 0.01 level,

A, river sediments; **B**, river water

There are strong positive correlation coefficients between the elements in river sediments as follows: Sb-Cu (0.806), Sb-V (0.891), Cu-V (0.83), Sb-Al (0.693), Al-V (0.565), Sb-Co (0.552), Al-Co (0.79), Hg-Mn (0.571), Sb-As (0.842), As-Cu (0.697), As-V (0.806), As-Al (0.717), As-

Co (0.818), Mn-Cd (0.705), V-Cd (0.62), Hg-Cd (0.668), Sb-Th (0.855), V-Th (0.758), Al-Th (0.809), Co-Th (0.879) and As-Th (0.915). The elemental associations in river sediments yielded moderate to strong positive correlations for Sb-Al-V-Co-As-Th and Sb-Mn-V-As-Cu-Hg-Cd groups. Elements in river water samples showed strong positive correlation coefficients between themselves as follows: Sb-Mn (0.558), Mn-Cu (0.648), Sb-V (0.758), Mn-V (0.867), Mn-Al (0.77), Sb-Co (0.733), Mn-Co (0.818), V-Co (0.842), Sb-Hg (0.863), As-Mn (0.745), As-Cu (0.806), As-Al (0.782), Mn-Cd (0.748), V-Cd (0.608), Al-Cd (0.827), Co-Cd (0.669), As-Cd (0.62), Sb-Th (0.774), Mn-Th (0.927), V-Th (0.902), Al-Th (0.756), Co-Th (0.787), As-Th (0.591) and Cd-Th (0.755). In general, there existed moderate to strong positive correlations within the elements in the two groups of elements below:

Sb-Mn-V-Co-As-Hg-Cd-Th, and Sb-Mn-Cu-V-Al-Co-As-Cd-Th

The correlation coefficients between river water - sediment relationship (Table 4.19) showed strong positive correlations for 70% of the examined elements (Mn, Cu, V, Al, Hg, As and Cd). Sb, Co and Th, however, showed weak positive correlations in the water-sediment relationship.

Table 4.19: Spearman's correlation for water-sediment in Angonabeng and Bediabewu rivers

Element	Correlation coefficient
Sb	0.018
Mn	0.685*
Cu	0.600*
V	0.745**
Al	0.608*
Co	0.176
Hg	0.927**
As	0.976**
Cd	0.729**
Th	0.341

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level

4.5.2. Springs

(a) Concentrations of heavy metals in spring water and sediments samples

The mean concentrations of the 10 examined elements (Sb, Mn, Cu, V, Al, Co, Hg, As, Cd and Th) in water and sediment samples from three springs (one from Mile 7 and two from Teberebie) are presented in Table 4.20. For the spring water samples, Teberebie springs (2 and 3) recorded a higher average Sb concentration of 8.38ppm and 9.43ppm, respectively while the Mile 7 spring registered 3.69ppm. The spring sediment samples from Teberebie registered higher average deposits of Sb (20.97–33.6ppm). The average Sb concentration in Mile 7 spring sediment samples was 5.29ppm. Teberebie spring 3 water samples had the highest Mn concentration of 21.2ppm and the lowest (6.25ppm) was recorded at Mile 7 spring water.

The Mn concentration in sediment at Teberebie spring 3 was the highest (117770ppm) and Mile 7 spring sediment samples had the least average level of 55.9ppm. Mile 7 spring water samples had the highest average Cu concentration of 4.65ppm, the two Teberebie springs had the least average concentration of between 0.35 and 0.514ppm. Average concentrations of Cu in spring sediments were 2.92ppm, 2.08ppm and 29.9ppm for Mile 7 spring, Teberebie spring 2 and 3 respectively.

The average V concentrations in both Mile 7 and Teberebie spring water samples were all less than 1ppm, and were found to be in the range of 0.166 and 0.632ppm. However, there were high deposits of V in the sediments of all the springs. Teberebie spring 3 sediments had the highest average V concentration of 1201ppm and Mile 7 spring recorded the least concentration of 58.8ppm.

Table 4.20: Average values (ppm) of heavy metals in springs of Mile 7 and Teberebie

	Mile 7 Spring 1		Teberebie Spring 2		Teberebie Spring 3	
	Sediment	Water	Sediment	Water	Sediment	Water
Sb	5.29±8.18	3.69±2.3	20.97±15.7	8.38±2.94	33.6±11.7	9.43±1.93
Mn	55.9±13.8	6.25±4.82	189.2±54.9	20.7±3.29	117770±188297	21.2±1.01
Cu	2.92±3.12	4.65±0.81	2.08±0.59	0.35±0.09	29.9±13.9	0.514±0.12
V	58.8±44.1	0.278±0.08	230.2±21.4	0.166±0.08	1201±341	0.632±0.78
Al	8475±1166	17.6±0.929	10890±1218	19.3±1.98	142260±11244	27.3±2.09
Co	5.15±0.342	14.4±0.847	5.15±0.34	0.498±0.16	143±65.2	0.584±0.15
Hg	ND	ND	0.06±0.02	0.014±0.01	0.01±0.01	ND
As	1.65±0.57	0.206±0.07	1.94±1.0	0.22±0.12	1.06±0.27	1.29±0.46
Cd	ND	ND	0.204±0.03	0.024±0.02	0.434±0.296	0.656±0.52
Th	23.3±39.3	0.148±0.05	16.98±6.21	1.55±0.39	34.1±17.2	2.03±0.74

ND implies below detection

The results revealed high amount of Al in Teberebie springs. Teberebie spring 3 water and sediment samples recorded the highest Al concentrations of 27.3 and 142260ppm, respectively whereas Mile 7 spring water and sediment samples registered the lowest levels of 17.6 and 8474ppm, respectively.

The result revealed that even though Teberebie spring sediments recorded a higher average concentration of Co (5.15–143ppm), they had the least Co concentrations in water (0.498–0.584ppm). Mile 7 spring sediment and water samples recorded average Co concentrations of 5.154 and 14.42ppm, respectively. The Hg and Cd were not detected in both water and sediment samples from Mile 7 spring. However, Teberebie spring 2 water and sediment samples recorded average Hg concentrations of 0.014ppm and 0.06ppm, respectively. No Hg was detected in Teberebie spring 3 water samples; however, the level in sediment samples was found to be

0.01ppm. The average Cd concentrations in Teberebie springs 2 and 3 water samples were detected to be 0.024 and 0.656ppm, respectively. The amount of Cd levels in Teberebie Springs 2 and 3 sediments were 0.204 and 0.434ppm, respectively.

The As concentrations in all spring samples were less than 2ppm. Mile 7, Teberebie springs 2 and 3 recorded average As concentrations in water samples of 0.206, 0.22 and 1.29ppm, respectively, and that of the sediments were 1.65, 1.94 and 1.06ppm, respectively. The average Th concentrations in Mile 7 spring, Teberebie springs 2 and 3 water samples were detected to be 0.15, 1.55 and 2.03ppm, respectively. The highest average Th concentration of 34.1ppm occurred in Teberebie spring 3 sediments whereas Teberebie spring 2 sediment samples had the least average concentration of 16.98ppm.

In general, the ranking of elements in spring water samples in terms of concentrations was as follows: **Al>Mn>Sb>Co>Cu>Th>As>V>Cd>Hg**. The ranking of elements in spring sediment samples with respect to concentrations followed the order as shown below: **Al>Mn>V>Co>Th>Sb>Cu>As>Cd>Hg**. A comparative diagram of elements in spring water and sediments is shown by Fig. 4.20-Fig.4.24.

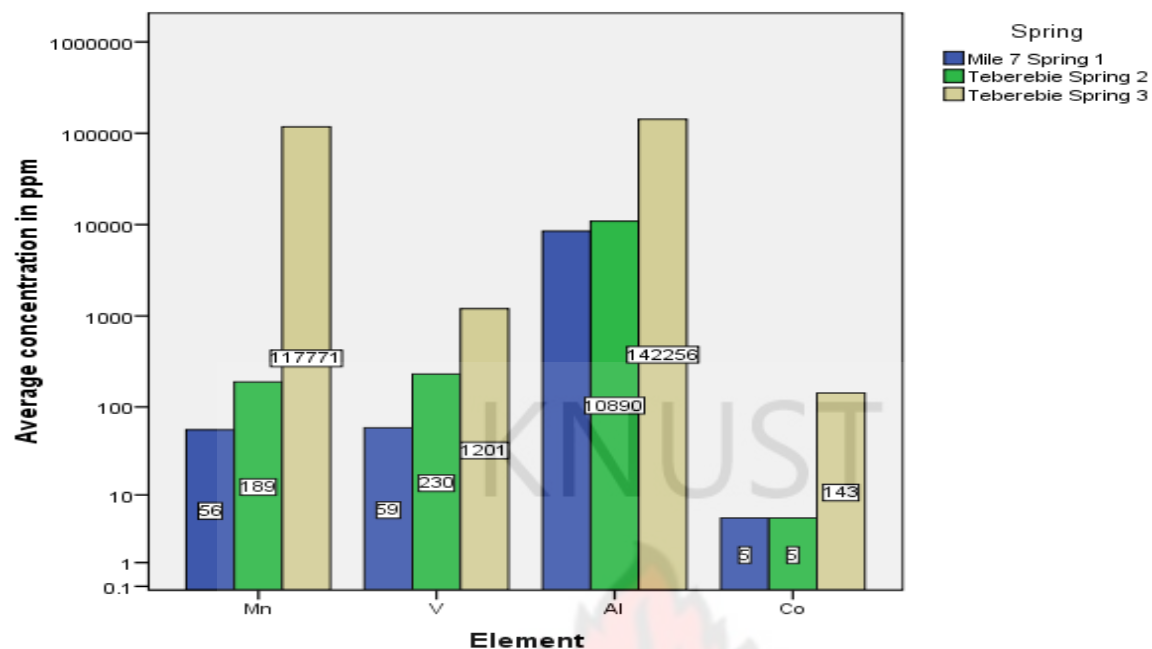


Fig.4.21: Variations of Mn, V, Al, and Co in Mile 7 and Teberebie springs sediments

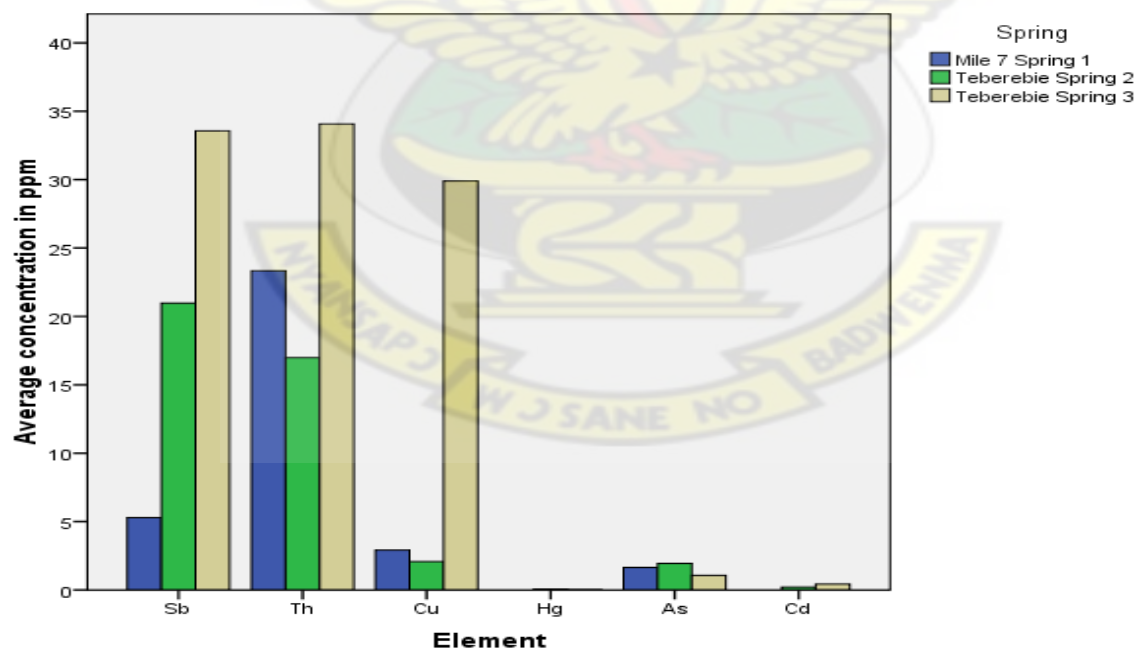


Fig.4.22: Variations of Sb, Th, Cu, Hg, As and Cd in Mile 7 and Teberebie springs sediment

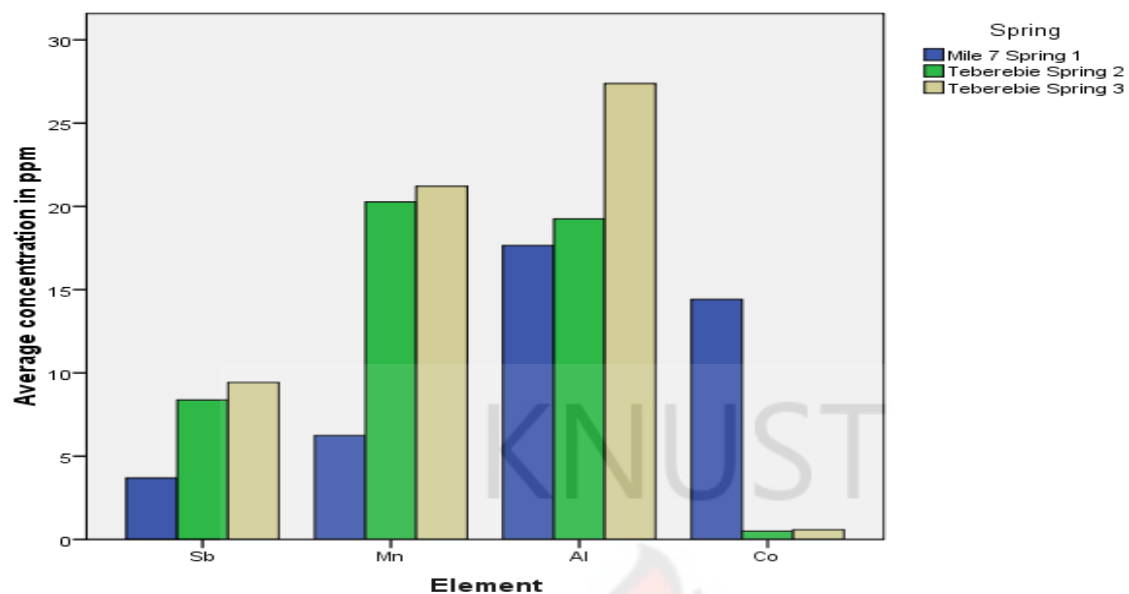


Fig.4.23: Variations of Sb, Mn, Al, and Co in Mile 7 and Teberebie spring water samples

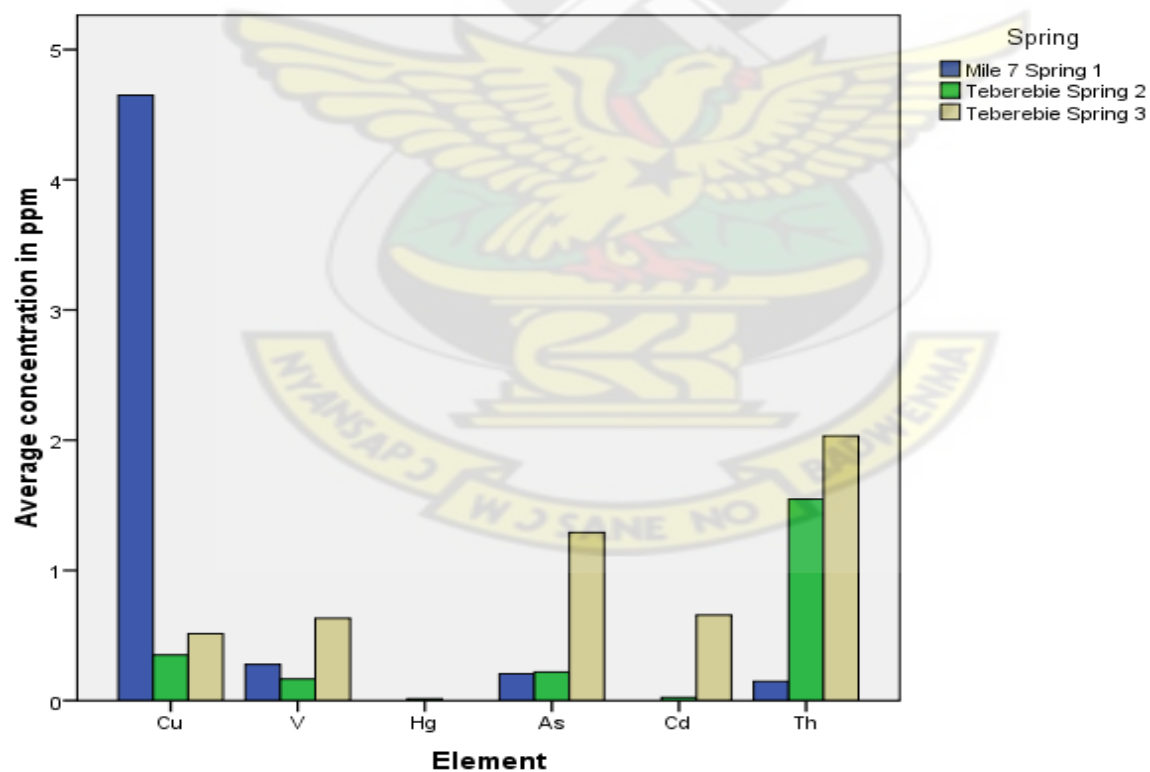


Fig.4.24: Variations of Cu, V, Hg, As, Cd and Th in Mile 7 and Teberebie springs water samples

(b) Elemental relationships in spring water and sediment samples

The correlation coefficients (Table 4.21) of the elements in the examined springs of the study area demonstrates good inter-relationships between Sb, Mn, Cu, V, Al, Co, Hg, As, Cd and Th. The strong positive correlation coefficients for the paired elements in spring sediments were as follows: Sb-Mn (0.893), Sb-Cu (0.793), Sb-V (0.900), Cu-V (0.832), Sb-Al (0.893), Al-V (0.971), Sb-Co (0.723), Al-Co (0.805), As-Hg (0.740), Sb-Th (0.811), V-Th (0.739), Al-Th (0.729) and Co-Th (0.741). Mercury showed negative significant correlation with all the elements except Arsenic and Cd showed weak correlations with Sb, Mn, Cu, V, Al, Co and Th (Table 4.22). The elemental associations in spring sediments produced two groups showing a moderate to strong significant positive correlations. These groups of elements are Sb-Mn-V-Al-Cu-Co-Cd-Th and Sb-As-Hg-Th.

Elements in spring water samples showed strong positive significant correlation coefficients as follows: Sb-Mn (0.899), Mn-Al (0.764), V-Co (0.445), As-Mn (0.717), As-Al (0.667), Cd-Cu (0.669), Al-Cd (0.826), Co-Cd (0.569), As-Cd (0.66), Sb-Th (0.733), Mn-Th (0.77), Al-Th (0.756), and As-Th (0.62). From Table 4.22, there were significant negative correlation coefficients for the following element pairs; Cu-Mn (-0.462), Th-Cu (-0.655) and Th-Co (-0.729). In general, there was a moderate to strong positive correlations for the following groups of elements: Sb-Mn-Al-As-Hg-Cd-Th and Cu-Co-V.

Table 4.21: Spearman's correlation for water-sediment in springs of the study area

Element	Correlation coefficient
Sb	0.876**
Mn	0.864**
Cu	-0.029
V	0.133
Al	0.807**
Co	-0.018
Hg	0.444
As	-0.292
Cd	0.281
Th	0.484*

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level.

Table 4.22 is a correlation matrix of the 10 examined elements in spring water-sediment relationship. The correlation coefficients between spring water and sediment (Table 4.21) showed strong positive correlations for 40% of the examined elements (Sb, Mn, Al and Th). Vanadium, Hg, and Cd, however, showed weak positive correlations in the water-sediment relationships. Cu, Co, and As concentrations in springs showed negative correlation in the water-sediment relationship.

Table 4.22: Correlation matrix of heavy metals in spring sediments and water samples from Mile 7 and Teberebie

A	Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th
Sb	1									
Mn	0.893**	1								
Cu	0.793**	0.832**	1							
V	0.900**	0.982**	0.832**	1						
Al	0.893**	0.961**	0.821**	0.971**	1					
Co	0.723**	0.755**	0.863**	0.780**	0.805**	1				
Hg	-0.182	-.707*	-.707*	-.727**	-.701*	-.707*	1			
As	0.089	-0.271	-0.161	-0.229	-0.3	-0.23	0.740**	1		
Cd	0.091	0.43	0.164	0.285	0.261	0.44	-0.058	-0.06	1	
Th	0.811**	0.743**	.782**	0.739**	0.729**	0.741**	-0.311	0.125	0.527	1

B										
Sb	1									
Mn	0.899**	1								
Cu	-0.404	-.462*	1							
V	0.05	0.05	0.389	1						
Al	0.820**	0.764**	-0.337	0.014	1					
Co	-0.356	-0.436	0.875**	0.445*	-0.33	1				
Hg	0.289	0.289	0.577	0.296	0	-0.29	1			
As	0.724**	0.717**	0.004	0.304	0.667**	-0.11	.889*	1		
Cd	0.667*	0.343	0.669*	0.483	0.826**	0.569*	-0.304	0.660*	1	
Th	0.733**	0.770**	-.655**	-0.078	0.701**	-.729**	0.577	0.620**	0.171	1

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level

A, Spring sediment; B, Spring water

4.5.3 Contamination degrees of stream water samples

The contamination degrees of the monitored streams are presented in Table 4.23. Angonabeng river water column recorded the highest contamination degree value of 9695 for the elements Sb, Mn, Al, Hg, As and Cd. Bediabewu river followed with contamination degree value of 4090. Teberebie spring 3, 2 and Mile 7 spring water registered contamination degree values of 1003, 603 and 779, respectively.

Generally, the contamination degrees of riverine water were higher than that of springs. This is shown by Fig. 4.24.

Table 4.23: Contamination degrees (C_d) of streams for the elements Sb, Mn, Cu, Al, Hg, As and Cd

Stream	C_d
Mile 7 Spring 1	779
Teberebie Spring 2	603
Teberebie Spring 3	1003
Angonabeng River	9695
Bediabewu River	4090

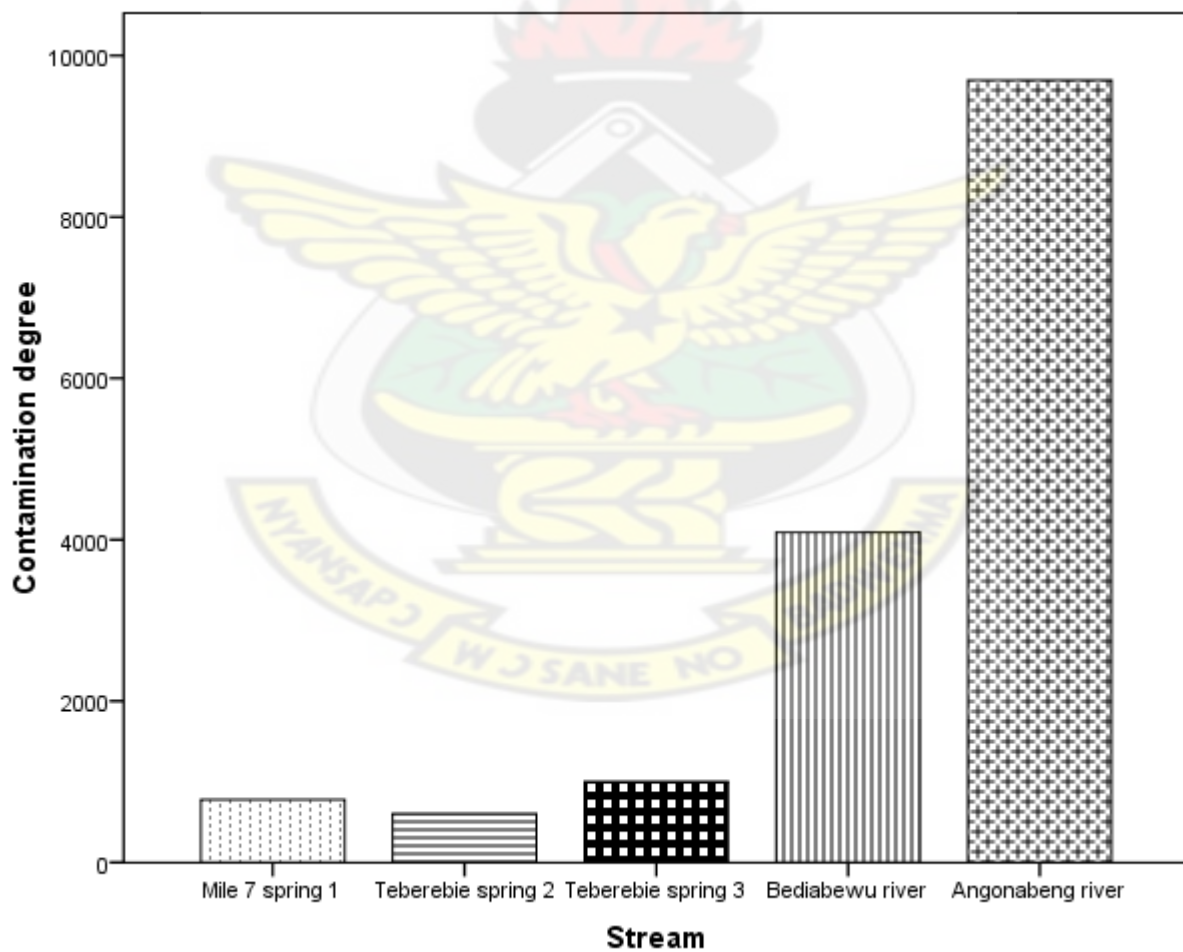


Fig. 4.24: Comparison of contamination degrees of stream water samples

4.5.4 Quantification of stream sediments pollution

The CFs and PLIs of the Angonabeng and Bediabewu rivers are shown in Table 4.24.

Table 4.24: Contamination factors (CFs) and Pollution Load Indices (PLIs) of streams sediments

	Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th	PLI
Teberebie Spring 2	13.98	0.223	0.046	1.77	0.136	0.181	0.15	0.149	0.68	1.42	0.41
Teberebie Spring 3	22.4	138.6	0.664	9.24	1.78	5.01	0.025	0.081	1.45	2.84	2.1
Mile 7 spring 1	3.53	0.066	0.065	0.451	0.11	0.181	-	0.127	-	1.945	0.276
Angonabeng River	25.9	42.9	0.289	1.02	1.08	0.07	0.53	0.415	2.19	0.136	1.1
Bediabewu River	205.9	0.429	0.448	3.21	2.15	0.702	0.135	1.03	1.04	1.31	1.43
Kakum river	2.15	0.914	0.071	0.236	0.197	0.272	-	0.03	-	0.0001	0.09

The CFs result shows that all the streams have high levels of Sb in their sediments in the order:

Bediabewu river (205.94)> Angonabeng river (25.9)>Teberebie spring 3 (22.4)>Teberebie spring 2 (13.98)>Mile 7 spring (3.53)>Kakum river (2.15). Teberebie spring 3 sediment recorded the highest CF value of 138.6 for Mn whereas Angonabeng river garnered a CF value of 42.9. Teberebie spring 2, Mile 7 spring as well as Kakum river registered Mn CF values less than 1.0. The highest CF value (9.24) for V was found at Teberebie spring 3 sediment samples. The CF values of V recorded for Bediabewu river, Teberebie spring 2 and Angonabeng river sediments were 3.2, 1.77 and 1.02, respectively. Mile 7 spring and Kakum river recorded CF values less than 1.0 for V. Bediabewu river had the highest CF value for Al (2.15) and Teberebie spring 3 followed with 1.78. Mile 7 spring and Kakum river recorded CFs for Al less than 1.0. Teberebie spring 3 recorded the highest (5.01) CF value for Co. The rest of the stream sediments recorded CF values less than 1.0 for Co.

The highest CF for Cd (2.19) was detected in Angonabeng river. The CF values for Cd for Teberebie spring 3 and Bediabewu river sediments were computed to be 1.45 and 1.04,

respectively. Teberebie spring 2 showed Cd CF of 0.68. Apart from Bediabewu river which retained As CF value slightly above 1 (1.03), all the rest of the examined streams had values less than 1.0. Teberebie spring 3 recorded the highest Th CF value of 2.84 , followed by Mile 7 spring (1.945) and Teberebie spring 2 (1.42), respectively. Angonabeng and Kakum rivers had Th CF values less than 1.0 for their sediments. All the streams recorded CF values less than 1.0 for Cu and Hg.

The overall Pollution Load Indices for the stream sediments were found to be in the order: Teberebie spring 3 (PLI = 2.1) > Bediabewu river (PLI = 1.43) > Angonabeng river (PLI=1.1) > Teberebie spring 2 (PLI = 0.41) > Mile 7 spring1 (0.276) > Kakum river (PLI = 0.09).

A comparative diagram of the PLI values in stream sediment samples is presented by Fig.4.26.

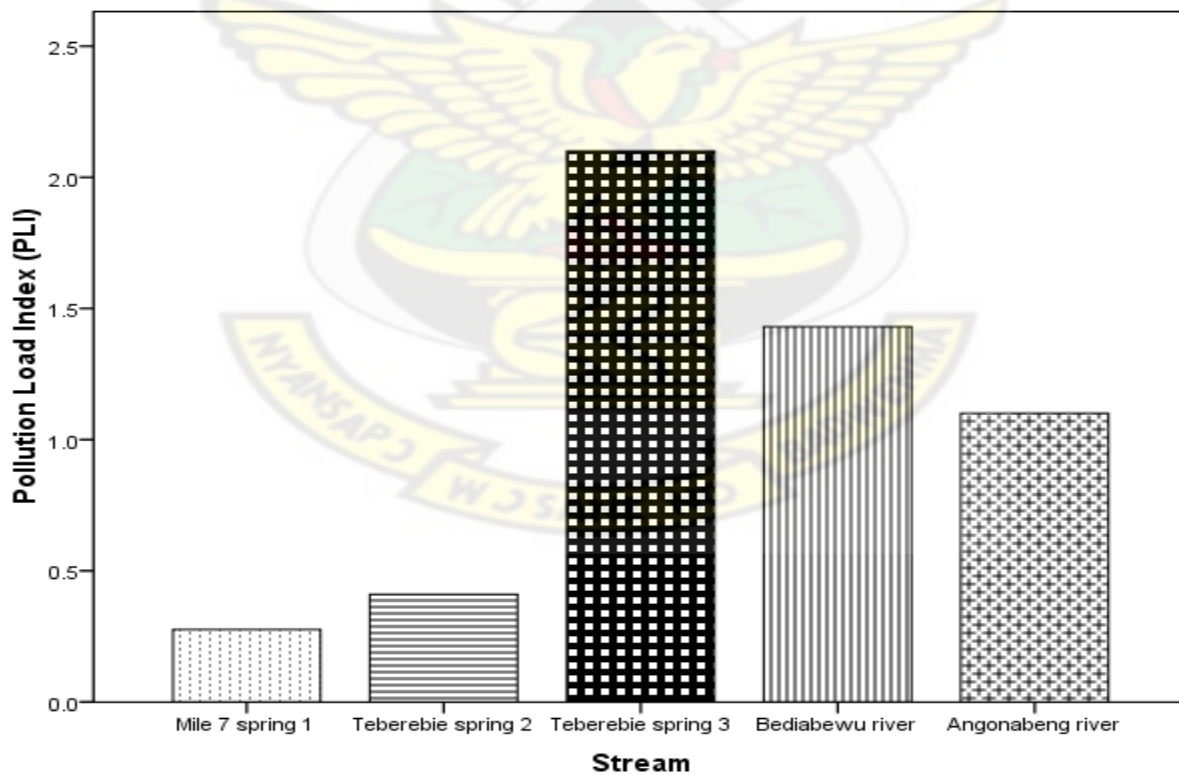


Fig.4.26: Comparison of Sediment Pollution Load Indices of examined streams.

The geoaccumulation indices and enrichment factors for the streams are presented in Table 4.25 and Table 4.26 respectively.

Table 4.25: Geoaccumulation Index (Igeo) of stream sediments

	Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th
Teberebie Spring 2	3.22	-2.75	-5.02	0.239	-3.46	-3.05	-3.32	-3.33	-1.14	-0.08
Teberebie Spring 3	3.89	6.53	-1.17	2.62	0.245	1.74	-5.91	-4.19	-0.05	0.921
Mile 7 Spring 1	-1.88	-4.51	-4.53	-1.73	-3.82	-2.47	-	-3.56	-	0.375
Angonabeng River	4.11	4.84	-2.38	-0.549	-0.47	-3.77	-1.5	-1.85	0.548	-3.46
Bediabewu River	7.1	-1.81	-1.74	1.1	0.522	-0.51	-3.47	-0.543	-0.53	-0.195
Kakum River	0.521	-0.71	-4.39	-2.67	-2.92	-2.46	-	-3.9	-	-0.479

The Igeo values (Table 4.25) revealed that nearly all the profiles for Cu, Al, Co, As, Hg, Cd and Th fell into class 1 (Table 4.9). The Igeo values for Cu, Co, Hg and As for all the streams are <0 , indicating practically unpolluted stream sediments with respect to these metals. The Igeo values for Th for Teberebie spring 3 and Mile 7 spring were >0 but <1 indicating unpolluted to moderately polluted sediments.

The Sb Igeo values for the streams varied most, ranging from -1.88 to 7.1 . Bediabewu river sediments recorded the highest Sb Igeo value of 7.1 and falling into the category ‘very strongly polluted’ sediment with Sb. Teberebie spring 2 and 3 showed Sb Igeo values of 3.22 and 3.89 , respectively. This puts them into Igeo class 5 (strongly polluted) while Angonabeng river had an Igeo value of 4.11 hence classified as strongly to very strongly polluted with respect to Sb concentration.

With the exception of Teberebie spring 3 and Angonabeng river, all the rest of the examined streams recorded Igeo <0 for Mn. Teberebie spring 3 and Angonabeng river recorded Mn Igeo of

6.53 and 4.84 respectively. Angonabeng river and Teberebie spring 3 are placed in strongly to very strongly polluted with regards to Mn concentration. Beside Teberebie springs and Bediabewu river, the rest of the streams registered V Igeo of <0. Teberebie spring 3 recorded the highest V Igeo of 2.62 and Bediabewu river had 1.1, pitching these water bodies into Igeo classes 3 and 4, moderately to strongly polluted respectively. All the streams recorded Al Igeo of <0 except Bediabewu river and Teberebie spring 3, which had 0.522 and 0.245 respectively. Therefore all the streams are practically unpolluted whist Bediabewu river and Teberebie spring 2 are unpolluted to moderately polluted with respect to aluminium. With exception of Angonabeng river with Cd Igeo value of 0.548, all the examined streams had Cd value of less than 0 and therefore classified as practically unpolluted while Angonabeng is unpolluted to moderately polluted. The Co Igeo values for all, except Teberebie spring 3, were <0. Teberebie spring 3 sediments was in the Igeo class 3 (moderately polluted) with a value of 1.74.

Table 4.26: Enrichment Factors for stream sediments of study area

	Sb	Mn	Cu	V	Co	Hg	As	Cd	Th
Teberebie spring 2	102.7	1.63	0.339	13.01	0.127	1.1	1.09	4.99	10.39
Teberebie spring 3	12.6	77.9	0.374	5.19	2.82	0.014	0.046	0.813	1.59
Mile 7 spring 1	33.3	0.62	0.612	4.27	2.56	0	1.2	0	18.4
Angonabeng river	23.9	39.7	0.268	0.949	0.102	0.491	0.385	2.03	0.123
Bediabewu river	95.6	0.199	0.208	1.49	0.499	0.063	0.478	0.483	0.608

The results showed that all the stream sediments are significantly enriched with Sb with EF range of 12.6–95.63. All the stream sediments with respect to Cu, Co, Hg and As have enrichment factors of less than 3 and can therefore be classified as depleted to minimally enriched with respect to these elements. Mile 7 spring and Bediabewu river, appeared to be significantly enriched with Mn. The highest EF value of 77.9 for Mn was recorded in Teberebie

spring 3. Cobalt appeared to be enriched in spring sediments than in riverine sediments. The EF values of Co for Teberebie spring 3, 2 and Mile 7 spring were 2.82, 0.127 and 2.56, respectively. The riverine sediments of the study area recorded EFs less than 1.0 for Co. The spring sediments were significantly enriched in V than rivers. The EF ranges of V for spring and river sediments were 4.27–13.01 (moderately enriched) and 0.94–1.49 (depletion to minimal enrichment), respectively.

Thorium was significantly enriched in Mile 7 spring and Teberebie spring 2 sediments with EF values of 18.4 and 10.39, respectively. The rest of the streams recorded EF values less than 3 for Th. All the streams except Teberebie spring 2 were depleted to minimal enrichment with Cd, as revealed by their EF values (<3). Teberebie spring 2 recorded the highest EF value of 4.99, followed by Angonabeng river with 2.03.

4.6 BOREHOLES

4.6.1 Concentrations of heavy metals in boreholes

The INAA results for borehole water samples are presented in Table 4.27. The levels of Sb, Cu, Hg, Cd and Th in all the borehole water samples were less than the detection limits. Fig. 4.26 is a comparative diagram of the levels of Mn, V, Al, Co and As in Mile 7 and Teberebie boreholes.

Table 4.27. INAA results for heavy metal levels (ppm) in borehole water samples from Mile 7 and Teberebie

	Mile 7 Borehole 1	Mile 7 Borehole 2	Teberebie Borehole 3
Sb	ND	ND	ND
Mn	0.096±0.05	1.158±0.979	0.396±0.261
Cu	ND	ND	ND
V	0.13±0.028	0.324±0.462	0.634±0.256
Al	6.776±1.09	4.052±3.99	2.02±3.21
Co	0.15±0.219	0.164±0.233	0.496±0.317
Hg	ND	ND	ND
As	0.01±0.01	0.01±0.01	ND
Cd	ND	ND	ND
Th	ND	ND	ND
ND implies below detection limit			

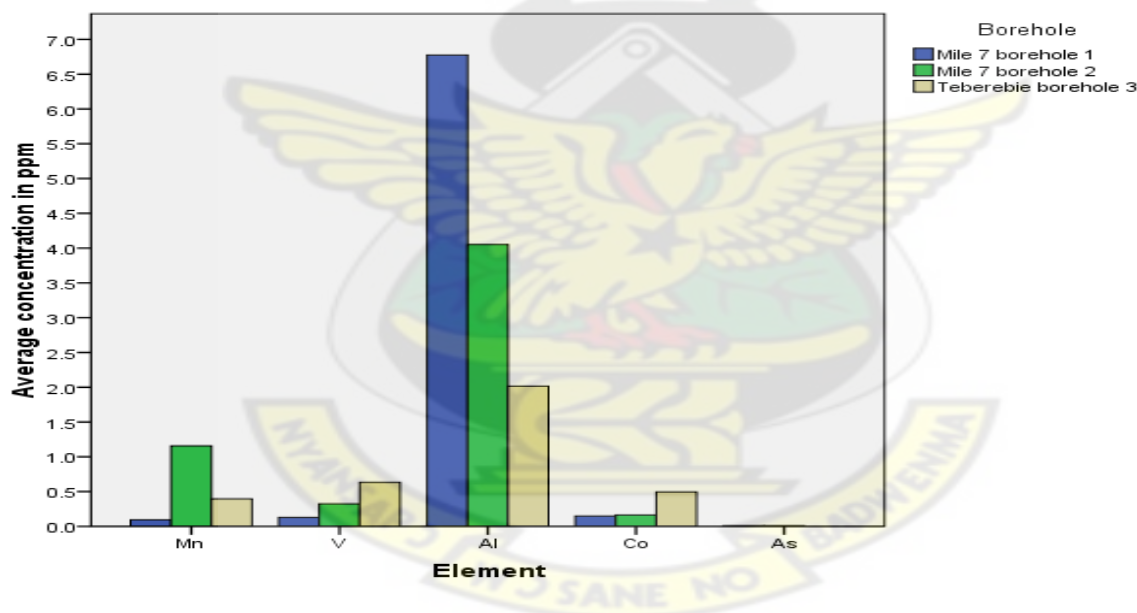


Fig. 4.26: Variations of Mn, V, Al, Co, and As in borehole water samples

In general, the average levels of Mn and Al were higher in Mile 7 boreholes than Teberebie borehole. However, Teberebie borehole recorded higher concentrations of V and Co than Mile 7 boreholes. Arsenic concentration of 0.01 was detected in Mile 7 borehole 1 and 2 while no arsenic was detected at the Teberebie borehole.

4.6.2 Relationships between Mn, V, Al and Co in borehole water

The result is presented in Table 4.28. The results revealed that there is no to weak correlation between V, Al and Co in the borehole water samples. However that was a strong positive correlation between Al and Mn for all the sampling points.

Table 4.28: Spearman's correlation matrix of elements in boreholes

Borehole		Mn	V	Al	Co
Mile 7 Borehole 1	Mn	1	-0.051	.900*	-0.205
	V	-0.051	1	-0.205	-.947*
	Al	.900*	-0.205	1	-0.103
	Co	-0.205	-.947*	-0.103	1
Mile 7 Borehole 2	Mn	1	0.616	0.900*	0.051
	V	0.616	1	0.462	-0.237
	Al	0.900*	0.462	1	0.154
	Co	0.051	-0.237	0.154	1
Teberebie Borehole 3	Mn	1	0.564	0.975	0.300
	V	0.564	1	0.711	0.410
	Al	0.975*	0.711	1	0.359
	Co	0.3	0.41	0.359	1

*. Correlation is significant at the 0.05 level (2-tailed).

CHAPTER FIVE

DISCUSSION

5.1 LICHENS

5.1.1 Lichen samples collection and soil contamination analysis using EF

To evaluate the contribution of soil to the elemental composition of the lichen due to contamination of samples, Enrichment Factor (EF) and Estimated Background concentration (EC) analyses were employed. This was necessary to test the efficiency of the method used in minimizing contamination of the lichen samples during the preparation stage and to evaluate the atmospheric contributions to the elemental levels in lichens as reported by Loppi *et al.* (1999).

It is shown that the EF values are far above 1.0 for all sampling sites for all the examined heavy metals (Table 4.15). The exceptions are sampling point 9 at Teberebie which had EF values for Cu and As to be 0.8 and 0.41, respectively. About 99% of the sampling points recorded EC values very closed to the measured concentrations. This result suggests that the washing of the lichen samples was very effective by the use of the de-ionized water and eliminated to a larger extent soil contamination. It may be inferred from the high EF and EC values that Sb, Mn, V, Co, Hg, Cd and Th are enriched in the lichens by active biological processes from atmospheric deposition, clearly indicating point and non-point origins of these elements. This conforms to the findings of Frontasyeva *et al.* (2004) and Nyarko *et al.* (2006). The high EF values for all sampling points for almost all examined elements may be attributed to the major mining activities dotted at the study area. The source of the high EF values for Th cannot be ascertained in relation to the mining activities. It may therefore be due to long distance atmospheric

deposition. Observation for Th could also mean that the enrichment in the atmosphere do not come from any pollution source. This also agrees with that of Bargagli (1995).

5.1.2 Pollution Source identification

(a) R-mode principal component analysis (PCA) of lichen data

The R-mode PCA revealed 2 latent factors. These factors were responsible for the data structure explaining 87.4% of the total variance of the dataset and possibly anthropogenic and natural origins. PC1 has the highest Eigenvalue of 3.775 (Table 4.5). The elements Sb, V, Al, Cu and Co registered factor loadings greater than 0.5 and constituted absolute loading values. PC1 may be interpreted as representing influences from anthropogenic sources mainly from the mining activities and the use of fertilizers by the farmers in the study area.

The second principal component PC2 was next in significance with an Eigenvalue of 2.498. As shown in Table 4.5, PC2 registered factor loading of 0.874 and 0.957 for the elements Cd and Th respectively. Cadmium has been identified as atmospheric and so some uncertainty exists due to the fact that it is essential for lichens. Therefore, it may occur in the stable form in the thallus of lichens as reported by Loppi *et al.* (1999). It has also been reported by Bargagli (1995) that Cd has low crustal abundance and may not likely be released by the soil. Thorium has been reported by Nyarko *et al.* (2004) not to be associated with ore body and therefore may unlikely be released into the environment through the mining operations in the study area.

The third principal component, PC3, had an Eigenvalue of 2.473 and was third in significance, explaining 24.727% of total variance. This pole had the elements Mn, Co, Hg, and As, as its

members. PC3 may also be attributed to point and non-point sources. Mining activities in the study area are the most likely anthropogenic point sources contributing to the presence of these metals in the local atmosphere. This is in conformity with the findings of Nyarko *et al.* (2004) at Obuasi gold mining area.

(b) R-mode cluster analysis (CA)

Cluster analysis (CA) used all the variance or information contained in the original lichen dataset. Ward's method was selected for element/sampling site classification because it possesses a small space distortion effect, uses more information on cluster contents than other methods, and has been proved to be extremely powerful grouping mechanism (Vega *et al.*, 1998).

To assess the affinity in terms of source of origin among the 10 examined elements, R-mode CA was performed on Al, As, Cd, Cu, Co, Hg, Mn, Sb, Th and V. The results revealed 3 distinct groups or clusters (Fig. 4.4).

The results obtained with the R-mode CA is similar to that of R-mode PCA groupings. The only difference is Co which in this analysis (R-mode CA) belongs to only one cluster, whereas in R-mode PCA, it is correlated with both PC1 and PC3. This may be so since CA considers all variance while PCA uses most variance and cluster members are distinct from members of other clusters. The results may suggest the same inference made on R-mode PCA that the two major sources of pollution in the atmosphere are the anthropogenic and natural. From the R-mode PCA and R-mode CA, the analysed metals may be classified into 3 groups with respect to source identification. Group 1, clustered by Sb, V, Al and Cu, may have resulted from both

anthropogenic activities (gold mining and agricultural activities) and natural sources. Group 2, clustered by Mn, Hg, Co and As, may have resulted from anthropogenic (gold mining) activities in the study area. The sources of Cd and Th (Group 3) are uncertain but are likely to be natural.

5.1.3 Spatial similarity and site grouping

(a) Q-mode cluster analysis (CA)

Q-mode CA was performed on lichen dataset to ascertain spatial similarities among the various sampling sites (Fig. 4.5). The results suggest that the sampling points belonging to a particular group share similar characteristics with respect to the analysed elements. The cluster analysis has, therefore, provided a useful classification of the lichen samples in the study area, which could be used to design an optimal future spatial monitoring network with lower cost. On the basis of the result from this work, the number of monitoring sites could be reduced and chosen only from groups 1 and 2.

(b) Q-mode principal component analysis (PCA)

The results show that Sb, Cu, V, Al and Co are important in lichens in 3 out of 4 sampling points located at Teberebie in the order SPLCH 7 > SPLCH 10 > SPLCH 9 (Table 4.6). This is not surprising since Teberebie community is sandwiched between the two main mines in the study area, and therefore is closer to the pollution source than the other communities (Mile 6, Mile 7 and Mile 8). As presented in Table 4.6, elements (Cd and Th) in PC2 of the R-mode PCA are most significant at sampling point SPLCH 3, located at Mile 7, and Mile 6 and Mile 8 sampling points.

The most significant pollution effects of Mn, Co, Hg and As (loaded on PC3) (Table 4.5) occurred at Mile 6 (SPLCH 1 and SPLCH 2) (Table 4.6). The PCA analysis shows that Sb, Cu, V, Al, Co, Cd and Th are more deposited in the atmosphere of Teberebie (SPLCH7, SPLCH8, SPLCH9 and SPLCH10) than Mile 6, Mile 7 and Mile 8. The control site is clearly differentiated from the sampling points in Teberebie and its environs, indicating the unpolluted nature of its atmosphere. The results from the Q-mode PCA suggest that atmospheric deposition of point source pollutants decrease with moving away from the pollution sources.

The Q-mode CA results are similar to that of Q-mode PCA. An exception is the listing of sampling point SPLCH8 (located at Teberebie) in cluster 1 of Q-mode CA (i.e., SPLCH5, SPLCH6, SPLCH1, SPLCH2, SPLCH3, SPLCH4 and SPLCH8) [Fig. 4.5]. This is not surprising since SPLCH8 sampling point is the closest to the other communities and may show some similarity in terms of air quality of the examined metals. In both Q-mode CA and R-mode PCA, the control sampling site is isolated from the rest of the sampling points.

The agreement existing between the CA and PCA multivariate statistical techniques reveals that the groupings of the sampling points have been performed in a quite convincing manner as stated by Simeonov *et al.* (2003). Group 1 consists of mainly lichen samples from Mile 6, Mile 7 and Mile 8 corresponding to relatively moderate pollution (MP) sites. Group 2 consists of samples from only Teberebie and corresponds to a relatively high polluted (HP) site. Group 3 (CONTROL which is not influenced by any gold mining activity) corresponds to relatively low polluted (LP) site.

5.1.4 Quantification of air pollution using lichens and Pollution Indices

Using the data generated from metals concentrations in lichens, sampling sites exposed to higher amounts of the pollutants were identified. Results as shown by Table 4.4 reveal that 100% of sampling sites registered PIF values greater than 3 (3.98–70.76) for Sb and V. This indicates the abundance of these two elements in the atmosphere of the study area and has reached heavily polluted status on the pollution scale.

With the exception of Mile 8 lichen sampling sites (SPLCH5 and SPLCH6), all the other communities recorded higher PIF values (81–622) for Hg. Mile 6 (SPLCH1 and SPLCH2) has the greatest pollution burden of As in the range of 22.48–80 on the PIF scale, followed by SPLCH 7 and SPLCH10 of Teberebie. The As concentrations in these sampling sites are high due to the pyrites and arsenopyrites associated with the ore body and the close proximity of the sites to the two mining sites. Mile 7 (SPLCH3 and SPLCH4), Mile 8 (SPLCH5 and SPLCH 6), and SPLCH 8 and SPLCH 9 of Teberebie show medium pollution status for As. These may be so since they are relatively farther away from the two main mining sites in the area. The study area, in general, is lightly polluted with Al, Co and Mn. The PIF values of Th for all sampling point are low and this may be due to the fact that Th is not associated with the gold ore body, and therefore unlikely to be released into the atmosphere. Mile 6, 7 and 8 are unpolluted with Cu but Teberebie is heavily polluted with this heavy metal. The mining activities could have contributed to the high concentrations of Cu at Teberebie.

The Pollution Load Index (PLI) for each community revealed that pollution load decreases as one moves away from the pollution sources. This is suggested because the closest communities

to the two main mines in the study area (Mile 6 and Teberebie) have the highest PIF values of 6 and 5.18, respectively (Fig. 4.1). Mile 8 which is virtually unaffected by the mining activities registered the least PLI value of 0.88.

5.2 SOILS

5.2.1 Elemental concentrations in soil samples

The levels of As, Cd, Co, Cu, Th and Hg in soil samples (Table 4.7) for all the sampling points are lower than soil quality having potential for harmful effects on human health or the environment (Table 2.2). The concentrations of these elements fall into the category of elemental levels in soils regarded as good quality soil according to the reference values (Table 2.2) given by VROM (1983).

Apart from Cd, all the examined elemental concentrations in the soil samples are within the normal soil range as reported by Bowen (1979) [appendix 5]. This reveals that the mining activities have not affected the soils of the study area greatly. The major source of the elements in the soils is most probably from the parent material and other point and non-point anthropogenic sources. The concentrations of V, Mn and Al are relatively higher in the soil samples. This is not surprising since these elements are principal components of the earth's crust. Their source is probably due to natural processes and anthropogenic activities in the area.

5.2.2 Quantification of soil pollution

The generally low concentrations of the elements in the soil samples are reflected in the overall Pollution Load Indices of the four communities (Table 4.8). The PLI values for all the

communities are less than 1.0. This suggest that mining activities in the vicinity of the study area have little impacts on the soil as far as the 10 examined elements are concerned. However, all the sampling points have contamination factor values above 5 for Cd. The trend for Cd contamination factors for the sampling points suggests that the mining activities contribution of Cd into the soils may be minimal. Other possible non-point sources such as agricultural and natural means may account for the levels in the soils.

5.2.3. Spatial similarity analysis of soil data

(a) R-mode and Q-mode Principal component analysis (PCA) for soil samples

The R-mode PCA revealed 2 latent factors responsible for the distribution patterns of element levels in soil samples (Table 4.13). These factors accounted for the structure of the data explaining 86.4% of the total variance of the dataset. These factors are possibly anthropogenic and natural origins.

PC1 has the highest Eigenvalue of 3.812. The elements Sb, Cu, V and Co recorded absolute factor loadings greater than 0.5 while As and Cd had absolute Eigenvalues less than -0.5. PC1 may be interpreted as representing influences from anthropogenic sources mainly from the mining activities and the use of fertilizers and agrochemicals by farmers in the study area.

The second principal component PC2 is next in significance with an Eigenvalue of 2.992. As shown in Table 4.13, PC2 registered factor loading of 0.61, 0.741, 0.862 and 0.95 for the elements V, Co, Hg and Th, respectively. These elements are suggested to have a similar pattern

in the soils throughout the sampling points. The pattern of V, Co, Hg and Th in the soil samples of the study area may show that the capacities of the soils to retain V, Co, Hg and Th may be identical. Their main sources are likely from parent materials and anthropogenic sources. As reported by Gordon *et al.* (2005), the relatively low levels of Hg in the soils may be attributed to organically bound forms of the metal derived from the atmosphere.

The third principal component, PC3, has an Eigenvalue of 1.84 and is third in significance explaining 18.398% of the total variance (Table 4.13). This pole has the elements Mn, Cu and Al as its members. PC3 may also be attributed largely to contribution from underlying bedrock of the soils and some non-point and point anthropogenic sources (mainly mining and agricultural chemicals). These elements are principal components of the earth's crust and their relatively high levels are not unexpected.

The results from Q-mode PCA show that concentrations of Sb, Cu, V, Co, As and Cd are relatively significant in soil samples at sampling points located at Teberebie in the order SPSL 9>SPSL 10 >SPSL 7>SPSL 8 with factor scores of 1.81, 0.86, 0.57 and 0.47, respectively (Table 4.14). This was not surprising since Teberebie community is located between the two main mines in the study area and therefore is closer to the pollution source than the other communities (Mile 6, Mile 7 and Mile 8). As shown in Table 4.14, V, Co, Hg and Th correlated with PC2 of the R-mode PCA are highest at sampling points SPSL 1 and SPSL 2 located at Mile 6. This community is also close to one of the mining plants in the study area and the elevated levels of V and Co may largely be due to the mining activities.

PC3 metals (Mn, Cu, and Al) are loaded at highest scores at sampling point SPLCH 7 stationed at Teberebie (Table 4.14). This sampling point is the closest to the mines at Teberebie and it is likely deposition from anthropogenic origin (mainly mining activities) is very prominent.

A plot of principal component PC1 versus principal component PC2 (Fig. 4.6) shows that the elements in these components namely Sb, Cu, V, Co, Hg, Cd, As and Th are more deposited in the soils of Teberebie (where SPSL7, SPSL 8, SPSL 9 and SPSL 10 are located) than the Mile 6, Mile 7 and Mile 8. The farthest community, Mile 8, is clearly located on a different quadrant of the diagram, indicating the relatively less effect of the mining activities on the soils of that community.

A plot of PC1 against PC3 also differentiated the communities as far as the elements in the PCs are concerned (Fig. 4.7). The results from the Q-mode PCA suggest that point source anthropogenic pollutants decrease with distance from the pollution source.

(a) R-mode and Q-mode Cluster Analysis (CA) of soil samples

The clusters and their members on the similarity distances from the CA are shown in Fig. 4.8 and Fig. 4.9. The CA result shows that the levels of V, Co, Sb, Al, Mn, Hg and Th in soil samples of Mile 6, Mile 7 and Mile 8 are different from those of Teberebie. It also reveals that As levels in soil samples from Teberebie are higher than the rest of the communities, suggesting proximity to the pollution source as major factor. The information given by R and Q-modes of CA shows that Teberebie community suffers most from the mining activities than Mile 6, 7 and 8.

5.4 STREAMS

5.4.1 Elemental concentrations in streams

For the water samples, the concentrations of Sb, Mn, Cu, Al, Co, Hg and As for Angonabeng and Bediabewu rivers are in the range of 10.74–41.44ppm, 8.04–17.804ppm, 3.67–5.6ppm, 13.78–14.64ppm, 2.3–4.1ppm, 0.52–1.48ppm and 12.18–18.59ppm, respectively (Table 4.17). Mining activities may have probably released extremely high levels of Sb, Mn, Cu, Al, Co, Hg and As into the environment, which were washed by rain water into these rivers. The relatively high levels of these elements could also be due to anthropogenic inputs, both point and non-point sources. Angonabeng and Bediabewu rivers are few miles away from the processing sites of the two major mines in the study area, and direct and indirect discharge of mine waste may be a contributing factor to the elevated levels of Sb, Mn, Cu, Al, Co, Hg and As in the water samples. These elements may have also entered the waterways through wet and dry deposition from air or through rain. According to Akabzaa and Darimani (2001) streams of the study area are actively used by illegal miners (popularly called *galamsey* operators) for their operations and these two examined rivers may not be exceptions. The high levels of these elements in the riverine water could also be due to the inherent mineralogy of the ores of the study area.

The Cd concentrations in the two rivers (Angonabeng and Bediabewu rivers) were almost the same (1.11ppm) and this may be attributed to natural occurrence of this element in the sediments and surrounding soils as well as the water of these rivers. It is also possible that Cd may have been washed into the rivers from agricultural chemicals used by farmers in the study area. This minimal spatial variation in cadmium concentrations in riverine water may be due to the conservative nature of this element in the aquatic system as shown by Karbassi *et al.* (2008). The

Sb, Mn, Cu, Al, Hg, As and Cd levels in Angonabeng and Bediabewu river water samples exceeded the WHO (2004) maximum allowable concentrations in drinking water. The relatively low concentrations of V and Th might be that tailings and soils rain-washed into the water bodies have low levels or no V and Th. Mining activities may probably release extremely low levels of V and Th into the environment, and water and sediment are unaffected by the mining activities with regard to the released V and Th.

For the water samples (Table 4.20), the concentrations of Sb, Mn, Cu, Al, Co, and As at Mile 7 and Teberebie springs are 3.69–9.43 ppm, 6.25–21.2 ppm, 0.35–4.65 ppm, 17.6–27.3 ppm, 0.498–14.4 ppm and 0.22–1.29 ppm, respectively. The reason for these high levels in spring water samples may be similar to that assigned to rivers. The concentrations of all these elements in the springs were relatively lower than those found in riverine water. This may be due to the water current in the rivers which causes regular interaction between the benthic zones and the littoral zones. There is virtually no movement in the spring waters and interaction between the bottom sediments and the water column is minimal.

The low levels of Th and V in the springs may be due to the fact that the soils washed into these water bodies contain low levels of these elements. The Hg and Cd levels in the Mile 7 spring were found to be below detectable limits. This could be due to the unavailability of these sources of water to illegal gold miners for use in the study area due to its proximity to the inhabitants of Mile 7 community. However, Teberebie spring 2 recorded some levels of Hg and Cd in its water samples. This may be due to the indiscriminate contamination of these springs by illegal miners in the study area. In general, the elemental concentrations in the Teberebie springs are higher

than Mile 7 spring water samples. The proximity of the Teberebie springs to the two gold mines as well as the likelihood for them to be used by illegal miners may be a contributory factor.

The riverine sediments showed the highest concentrations for all the monitored elements. The levels of Sb, Mn, Cu, V, Al, Co, Hg, As, Cd and Th are 38.86–309, 364.83–36468, 13.00–20.15, 86422.9–172274, 2.09–20.02, 0.054–0.21, 5.41–13.39, 0.31–0.66, and 1.64–12.91, respectively (Table 4.17). In general, the concentrations of the elements in the sediment samples are higher than that of the water and this might be due to the fact that metals can be either transported with the water or suspended sediment stored within the riverbed bottom sediment as reported by Adomako *et al.* (2008). Also, suspended sediments and metallic chemical solids are stored in riverbed sediment after they aggregate to form large denser particles that settle at the bottom of the water. The high levels of all the examined elements in riverine sediments is worrying since this may result in the reduction in the benthic biodiversity, where pollutant-tolerant species may probably take over the vacated niche as reported by Okweye *et al.* (2009). In addition, the high concentrations may serve as secondary pollution source even when the main pollution is reduced or eliminated.

It was also observed that the sediments of springs exhibited high levels of Sb, Mn, Cu, V, Co, As and Th. Teberebie springs recorded the highest levels probably due to their closeness to the pollution sources and sedimentation caused by soil erosions. In general, the levels of the examined elements in spring sediments are lower than in riverine sediments which may be due to the various drainage systems in the study area which are connected to the rivers.

5.4.2 Relationships between heavy metals in streams

The correlation matrix (Table 4.18) of the elements in riverine water samples demonstrates good inter-relationships between two groups of elements namely: Sb-Mn-V-Co-As-Hg-Cd-Th and Sb-Mn-Cu-V-Al-Co-As-Cd-Th groups. This relationship within the two groups suggests a common source of these elements into the water. The Sb-Mn-V-Co-As-Hg-Cd-Th group is likely to be anthropogenic inputs resulting from mine waste discharges into the river system and atmospheric depositions. The Sb-Mn-Cu-V-Al-Co-As-Cd-Th group might be from other point and non-point and natural sources. Al and Mn are major lithogenic elements and their association with other elements in the water column may indicate a natural origin probably from parent materials of bottom sediments.

Almost the same trend of elemental associations in riverine water was observed in spring water (Table 4.22). Two groups of elements emerged from the correlation analysis namely the Sb-Mn-V-Al-Cu-Co-Cd-Th and Sb-As-Hg-Th groups. The clustering of these metals may indicate the common sources of these elements. The Sb-As-Hg-Th group might be from anthropogenic sources since Hg is not a common component of the earth's crust. The Sb-Mn-V-Al-Cu-Co-Cd-Th group might have come from point and non-point natural sources.

The high correlation coefficients for elements in water-sediment in streams of the study area suggest that there is strong relationship between water and sediment element concentrations in the river and spring waters. With all the elements showing positive correlations (70% showing strong positive correlation coefficients) in riverine water-sediment, it can be inferred that the water current aided in the interactions between the water column and bed sediments. About 60%

of positive correlation coefficients (40% showing strong positive correlations) for springs suggest that the virtual stillness of the water bodies may have accounted for the differences with riverine water. Similar correlations between water and sediment levels have been reported from several global locations (Forstner *et al.*, 1990; Linnik, 2001; Karbassi *et al.*, 2008). The general strong correlation between element concentrations in water and sediment indicates the possibility of the sediments acting as secondary pollution source.

5.4.3 Contamination degrees (C_d) of streams

The contamination degrees have revealed that Angonabeng and Bediabewu rivers are heavily polluted with Sb, Mn, Cu, Al, Hg, As and Cd (Table 4.23). This is not surprising since these two rivers flow through the two mines of the study area, and are believed to be actively used by illegal miners for their operations. Teberebie springs are not left out in the operations of the galamsey operators. The closeness of the two sampled springs to the soil sampling points of Teberebie soils may account for the connections of the elemental levels in these samples. The soil samples have relatively high levels of these elements and due to soil erosion as well as run-off water it is likely these elements might get into the springs. Mile 7 soil samples have relatively low levels of Sb, Mn, Cu, Al and As, and that run-off due to soil erosion may contain low levels of these elements into these streams.

5.4.4 Quantification of stream sediment pollution

The Contamination Factor (CF) assessment of the quality of sediment has revealed that the Teberebie spring 2 is mainly polluted with Sb, Mn V, Al and Cd, and unpolluted to slightly polluted with Cu, Co, As, Hg and Th. This is likely to be the result of the closeness of the spring

to the mining plants. Mile 7 spring 1 sediment is mainly polluted with Sb, and slightly to unpolluted with Mn, Cu, V, Al, Co, Hg, As, Cd and Th (Table 4.24). This is not surprising since this spring is located far away from the probable anthropogenic pollution sources due to mining and agricultural chemicals. The general Pollution Loads (PLIs) of the Mile 7 spring 1 and Teberebie spring 2 are less than 1.0, suggesting the unpolluted nature of these springs with respect to the 10 examined elements. However, Teberebie spring 3 is heavily affected by anthropogenic and natural sources of the ten examined elements according to its PLI value (2.1).

Angonabeng river at Mile 6 and 7 is heavily polluted with Sb, Mn, V, Al and Cd. This same river is slightly polluted to unpolluted with Cu, Co, Hg and Th. The gross pollution of this river might be due to the proximity to the main pollution source and the indiscriminate use of this water body by illegal miners in the area. This river crosses the main mining untarred road linking Mile 6 to Mile 7, and massive settling of dust and other chemicals in the river could also contribute to its pollution. The overall Pollution Load Index of this river as far as the 10 examined elements are concerned is 1.1. This is regarded on the pollution scale as a progressive deterioration of the water quality. The Bediabewu river of Teberebie is also mainly heavily polluted with Sb, V, Al, As, Cd and Th, and slightly polluted to unpolluted with Mn, Cu, Co and Hg. This is likely as a result of the closeness of this river to one of the main mine plants at Teberebie. This river is also used by illegal miners in the area and their activities might be the cause of the elevated levels of these elements in the sediments of this river. The overall Pollution Load Index of this river is 1.43, slightly higher than PLI value for Angonabeng river. The results show that these two rivers are adversely affected by the mining activities in the study area. The Pollution Load Index (PLI) and the contamination degree (C_d) results have revealed that the amount of the examined

elements in the water column depends on the amount in the sediments, and they are directly proportional.

The Geoaccumulation Index (Igeo) calculations of the sediment samples have revealed the anthropogenic sources for some of the examined elements. The Igeo values for Mn and Sb for Teberebie spring 3 indicate that the springs are strongly polluted by these elements (Table 4.25). Teberebie spring 3 is moderately polluted with V and Co, as suggested by the Igeo values. The results also show the practically unpolluted status for all the water bodies with the elements; Cu, Al, Hg, As and Cd, and unpolluted to slightly polluted with Th. The Igeo values for all the elements for Mile 7 spring show practically unpolluted status of this water body with Al, As, Cd, Co, Cu, Hg, Mn, Sb and V and unpolluted to moderately polluted with Th.

The Angonabeng river is strongly to very strongly polluted with Sb and Mn, and also unpolluted to moderately polluted with Cd. The Igeo values also show that this river is practically unpolluted with Cu, V, Co, As, Al, Hg and Th. The Igeo values suggest that the Bediabewu river is very strongly polluted with Sb and unpolluted to moderately polluted with Al and V. This river is also shown to be practically unpolluted with, Co, Cu, Cd, Hg, As, Mn and Th.

The Enrichment Factor (EF) computation for the elements (Table 4.26) in Teberebie has revealed that Teberebie spring sediments are significantly enriched with Sb, Mn, V and Co. It also shows that these springs are depleted to minimal enrichment with Cu, Cd, As, and Th. Mile 7 spring sediments are also found to be significantly enriched with Sb, V and Th, and depleted to minimally enriched with Mn, Cu, Co, Hg, As and Cd. The EFs results show that the Angonabeng

river is significantly enriched with Sb and Mn, and depleted to minimally enriched with Cu, Co, V, Hg, Cd, As and Th. The Bediabewu river, on the other hand, is found to be significantly enriched with Sb and depleted to minimally enriched with Mn, Cu, V, Co, Hg, Cd, As and Th. The various enrichments of the elements in streams may be due to the mining activities and natural sources.

5.5 BOREHOLES

The high levels of Mn and Al in the borehole water samples from this study agree with some works done in the area by some previous researchers (Table 4.27). Akabzaa *et al.* (2001) and Asklund and Eldvall (2005) have reported high concentrations of Mn in some boreholes of the study area. Asklund and Eldvall (2005) reported high levels of Al in some wells of the study area. The occurrence of As in the Boreholes in Mile 7 is most probably natural and not considered a major problem in the area. Manganese and aluminium are all parts of common minerals and they probably originated from the parent rocks.

There are a number of reasons that may explain the low levels of Sb, Cu, Hg, Cd, As and Th values in boreholes. According to Asklund and Eldvall (2005) sorption processes are probably very important for metal concentrations of the groundwater in the area. Sorption can considerably lower the metal concentration in the groundwater (Asklund and Eldvall, 2005). All soil-types in the Tarkwaian rocks are clayey and the soils have a lot of adsorption and absorption sites due to their content of clay and abundance of Al/Fe oxides/hydroxides such as goethite and montmorillonite. Heavy metals such as Cu, Hg and Cd may be strongly bounded to these sites and this probably explains why Cu, Hg, As, Sb, Cd and Th show very low values. There is also

the likelihood that local mining pollutants such as the 10 examined elements have not yet reached the boreholes and that the groundwater quality will deteriorate in some of the boreholes in the future. The strong positive correlation between Mn and Al suggests that these elements may have a common origin.

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CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The application and use of biomonitors permit the study of pollution of areas where infrastructure for conventional assessment does not exist. The elemental concentrations of *in situ* epiphytic lichens (*Parmelia sulcata*) were obtained to map the distribution of heavy metals in the Teberebie, Mile 6, Mile 7 and Mile 8 communities of the Tarkwa gold mining area of Ghana and identify places with higher levels of the heavy metals concentration. The chemical analysis of lichen and surficial soil samples was performed by neutron activation analysis (NAA), and the results processed by multivariate statistical analysis and pollution indices analyses.

The pollution index factor (PIF) and pollution load index (PLI) analyses have revealed that the atmospheres of Teberebie, Mile 6 and Mile 7 have high levels of Sb, Mn, Cu, V, Al, Co, Hg, Cd and As in excess of the background values. This indicates that the abundance of these elements in the atmosphere of the study area has reached heavily polluted status on the pollution scale. It has been shown that the atmosphere of the communities deteriorates when one moves towards the mining sites. It may also be inferred from the enrichment factor (EF) and estimated background concentration (EC) analyses, computed using Al as a reference element, that Sb, Mn, V, Co, Hg, Cd and Th are enriched in the lichens by active biological processes from atmospheric deposition, clearly indicating point and non-point origins of these elements.

The principal component analysis (PCA) and cluster analysis (CA) have allowed the identification and assessment of pollution sources (i.e., anthropogenic and natural origin) of elements affecting air and soil quality in the study area. Both multivariate techniques, PCA and CA, led to very similar classification patterns. From the R-mode PCA and R-mode CA, the analysed elements in lichens may be classified into 3 groups with respect to source identification. Group 1, clustered by Sb, V, Al and Cu, may have resulted from both anthropogenic activities (gold mining and agricultural activities) and natural sources. Group 2, clustered by Mn, Hg, Co and As may have resulted from anthropogenic (gold mining) activities in the study area. The sources of Cd and Th (Group 3) are uncertain but are likely to be natural. The Q-mode CA and R-mode PCA clustered the lichen sampling sites into 2 significant statistical groups. The multivariate analysis has, therefore, provided a useful classification of the lichen samples in the study area, which could be used to design an optimal future spatial monitoring network with lower cost. On the basis of the result from this work, the number of monitoring sites could be reduced and chosen only from groups 1 and 2. Group 1 consists mainly of samples from Mile 6, Mile 7 and Mile 8, and corresponds to relatively moderate pollution (MP) sites. Group 2 consists of samples from only Teberebie and corresponds to a relatively high polluted (HP) site. The results from the Q-mode PCA suggest that atmospheric deposition of point source pollutants decrease when one moves away from the pollution sites.

This study supports the more extensive use of lichen as a bioindicator of atmospheric heavy metal pollution. Also, it serves as a reference for future studies on the assessment of the levels of toxic metal species in the Tarkwa gold mining area.

The levels of As, Cd, Co, Cu, Th and Hg in soil samples for all the sampling points are lower than reference values by provided by VROM (1983) and within the normal soil range reported by Bowen (1979). This shows that the mining activities have not affected the soils of the study area greatly. The generally low concentrations of the elements in the soil samples are reflected in the overall Pollution Load Indices of the 4 communities. The low PLI values for all the communities (less than 1.0) may suggest that the mining activities in the vicinity of the study area have little impacts on the soil as far as the 10 examined elements are concerned. The information given by PCA and CA from the soil data shows that Teberebie community suffers most from the mining activities than Mile 6, Mile 7 and Mile 8.

The results of this study have generally shown high levels of all the 10 examined elements in the streams water and sediment samples during the period the samples were studied. Angonabeng and Bediabewu rivers are few miles away from the processing sites of the two major mines in the study area, and direct and indirect discharge of mine waste may be a contributing factor to the high levels of Sb, Mn, Cu, Al, Co, Hg and As in the water samples. High concentrations of most of the heavy metals observed in almost all the streams may have a detrimental effect on the health of the inhabitants of the communities that use the river directly without treatment for domestic purposes.

The Contamination Factor (CF) assessment of the quality of sediments has revealed that the Teberebie springs are mainly polluted with Sb, Mn V, Al and Cd, and unpolluted to slightly polluted with Cu, Co, As, Hg and Th. Mile 7 spring sediment is mainly polluted with Sb, and slightly to unpolluted with Mn, V, Cu, Co, Al, Hg, As, Cd and Th. The general Pollution Load

indices (PLIs) of the Mile 7 spring 1 and Teberebie spring 2 are less than 1.0, suggesting the gross unpolluted nature of these springs with respect to the 10 examined elements. However, the Teberebie spring 3 is heavily affected by anthropogenic and natural sources, as indicated by its PLI value. The results show that Angonabeng and Bediabewu rivers are adversely affected by the mining activities in the study area. The water-sediment correlation matrix, Pollution Load Index (PLI) and the Contamination degree (Cd) results from this study have revealed that the amount of the examined elements in the water column depends on the amount in the sediments, and they are directly proportional.

The Enrichment Factor (EF) computation for the elements in Teberebie has revealed that Teberebie spring sediments are significantly enriched with Sb, Mn, V and Co. It also shows that these springs are depleted to minimally enriched with Cu, V, Cd, As, and Th. Mile 7 spring sediments are also found to be significantly enriched with Sb, V and Th, and depleted to minimally enriched with Mn, Cu, Co, Hg, As, and Cd. The EFs results show that the Angonabeng river is significantly enriched with Sb and Mn, and depleted to minimally enriched with Cu, Co, V, Hg, Cd, As and Th. The Bediabewu river, on the other hand, is found to be significantly enriched with Sb and depleted to minimally enriched with Mn, Cu, V, Co, Hg, Cd, As and Th. Attention is, therefore, being drawn to the fast degrading nature of the streams of the study area, which requires good environmental practices and constant monitoring to curtail any unanticipated disaster. Generally, the water quality of the studied boreholes with respect to the monitored elements can be said to be good.

This study has successfully demonstrated the usefulness of NAA supported by multivariate statistical analysis in monitoring and assessing the heavy metal pollution status in the Teberebie, Mile 6, Mile 7 and Mile 8 gold mining area. This research serves as a reference for future studies on the assessment of the levels of toxic metals in the study area. It is envisaged that the results of this study will enrich the discussion and understanding of the effects of mining activities on the environment as well as the health implications of people.

6.2 RECOMMENDATIONS

1. Efforts should be made by the mining companies in the area and the government to provide the people living along the Angonabeng and Bediabewu as well as Bonsa river with alternate sources of drinking water, such as sinking of boreholes.
2. Mining companies in the study area should be encouraged by environmental protection bodies (e.g., Environmental Protection Agency) to dispose tailings in a manner that optimizes protection of human safety and the environment.
3. Further investigations be conducted on the impact assessment of heavy metals in Bonsa river which has Angonabeng and Bediabewu rivers as its tributaries.
4. Efforts should be made by the mining companies in the study area, local authority and the government to tar the main roads in the Teberebie area to reduce dust generation.
5. A stricter environmental monitoring program which, among other activities, involves the re-vegetation of the area covered by the tailings piles and prohibiting unauthorized and unplanned digging of the tailings by the local people (galamsey operators) can reduce the process responsible for the leaching of the monitored elements from the tailings piles and their subsequent erosion into stream (springs and rivers).

6. Further studies are recommended in the area to provide information about the depth of the wells, the groundwater flow patterns, the location of small-scale mining activities and more detailed geological information of the sampling positions. These would give a better understanding of the processes governing the groundwater quality in the area.
7. It is recommended that multivariate statistical methods are integrated in future studies on pollution risk assessment of atmospheric, soil and water environment in Ghana.



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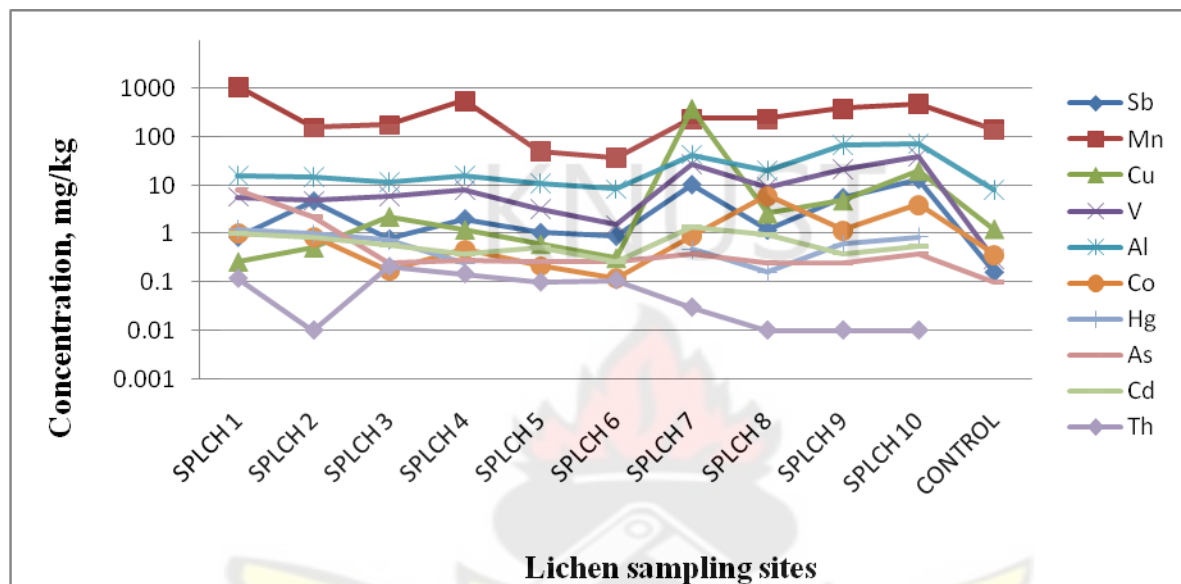
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APPENDICES

Appendix 1:

Pictorial impression of the element levels in lichens across the sampling points



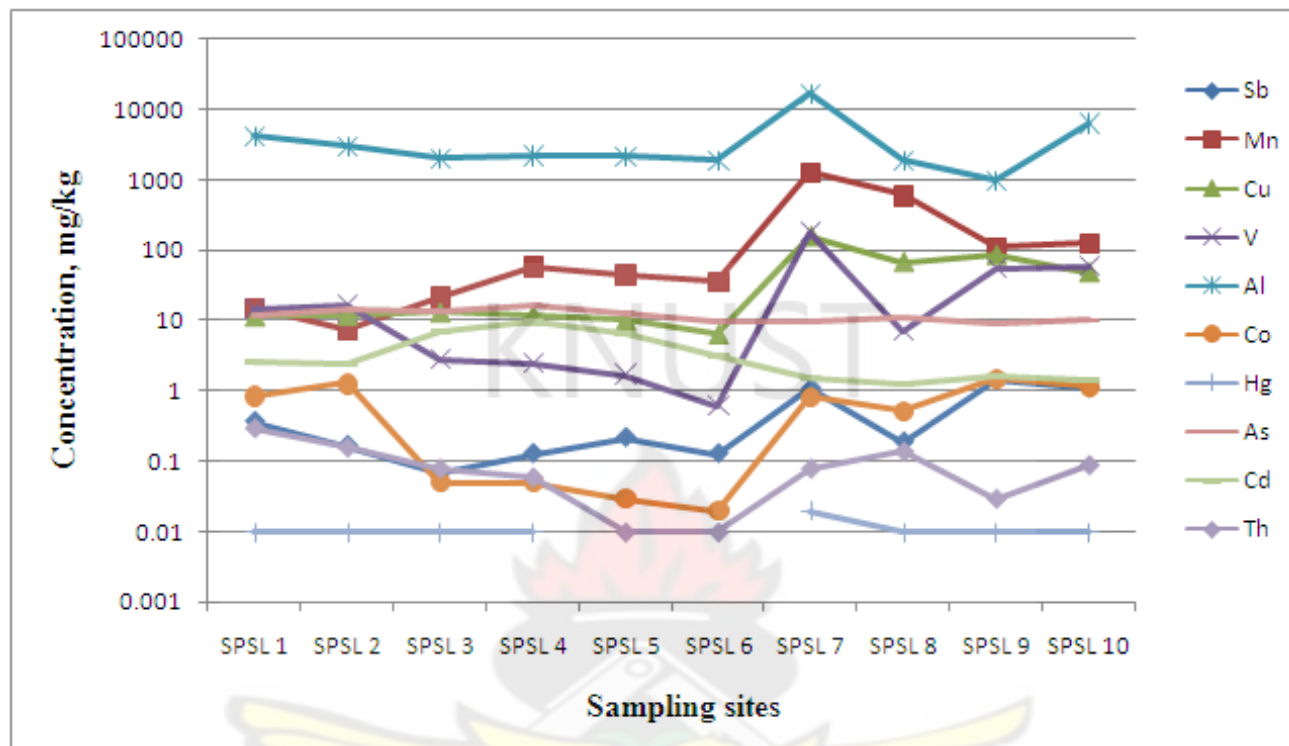
Appendix 2:

Average heavy metals values (ppm/dry weight) in lichens from the communities

	Mile 6	Mile 7	Mile 8	Teberebie	Control
Sb	2.79±5.59	1.409±1.81	0.968±0.396	5.03±5.93	0.158±0.100
Mn	627±1048	369±652	44.1±12.3	411±650	144±22.3
Cu	0.384±0.547	1.697±1.46	0.455±0.333	95.5±280	1.23±0.001
V	5.31±1.81	7.042±1.44	2.35±0.918	17.5±12.6	0.385±0.308
Al	15.2±3.95	13.905±3.48	9.62±1.64	37.9±23.7	8.00±10.5
Co	0.948±1.08	0.325±0.219	0.169±0.068	2.15±3.32	0.370±0.014
Hg	1.12±1.07	0.498±0.392	ND	0.405±0.278	ND
As	5.124±6.37	0.265±0.147	0.266±0.123	0.325±0.209	0.100±0.100
Cd	0.927±0.668	0.483±0.283	0.398±0.552	0.954±0.758	ND
Th	0.063±0.168	0.182±0.117	0.101±0.086	0.015±0.020	ND
ND implies not detected					

Appendix 3:

Distribution of elements in soil samples from sampling points



Appendix 4:

Average heavy metals (ppm/dry weight) in soil samples from the communities

	Mile 6	Mile 7	Mile 8	Teberebie	Control
Sb	0.268±0.147	0.100±0.049	0.171±0.220	0.954±0.590	0.508±0.531
Mn	11.5±5.64	40.7±23.2	41.117±7.68	530±918	36.8±34.2
Cu	11.6±5.76	12.4±5.34	8.215±2.42	89.1±72.5	5.99±3.02
V	15.6±5.02	2.69±1.03	1.16±0.655	76.0±163	3.78±3.33
Al	3668±1940	2144±180	2017±189	6523±9842	936±1309
Co	1.06±0.595	0.049±0.024	0.028±0.020	0.995±0.807	0.100±0.049
Hg	0.01±0.001	0.01±0.001	ND	0.013±0.011	ND
As	13.304±7.57	15.3±8.24	11.3±6.40	9.66±3.75	0.32±0.3.12
Cd	2.407±1.27	8.31±3.46	4.72±1.99	1.44±1.19	ND
Th	0.231±0.28	0.058±0.031	0.011±0.003	0.085±0.101	0.1±0.001
ND implies not detected					

Appendix 5:

World average shale (WA) and Normal soil Range (NSR) concentrations (ppm) of monitored elements

Std.	Sb	Mn	Cu	V	Al	Co	Hg	As	Cd	Th
WA**	1.5	850	45	130	80000	28.5	0.4	13	0.3	12
NSR*	0.2-10	20-10000	2-250	3-500	-	0.05-65	-	0.1-40	0.01-2	1- 35
* Normal soil element concentrations reported by Bowen (1979)										
**World average shale reported by Turakian and Wedepohl (1961)										

