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Table of Contents: Volume 11 Number 5 May 2017

ARTICLES

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Full Length Research Paper

Underscoring the role of Nigerian rural women in environmental protection: Lessons from Makarfi in Kaduna State, Nigeria

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Despite the role that rural women in Nigeria play in protecting the environment, not many studies acknowledge their contributions. As part of efforts to highlight women's contributions, this study interviewed 60 women between the ages of 20 to 60 on how important the environment is to their livelihood and how they protect it. Fifty percent (50%) of the women identified as farmers, forty percent (40%) as traders, three percent (3%) as housewives and seven percent (7%) identified as public servants. The participants reported that their activity under those capacities makes them interact closely with the environment; at different levels though. As part of efforts to protect their environment, these women engage in activities such as tree planting, manure application, sustainable harvesting and environmental sanitation as ways to give back to the environment. In their bid to protect their environment, the women face challenges such as poverty, cultural barriers, and the lack of government support. Policy makers are called upon to acknowledge the role of rural women in protecting the environment and include them in programmes surrounding conservation, disaster management, awareness campaign and rural development.

Key words: Environment, women, rural, protection.

INTRODUCTION

Women, especially in developing countries are said to work more closely with their environment because in most cases they rely on the environment for their subsistence (Glazbrook, 2011). Their interaction with the environment could be in form of subsistence farming, cleaning, or other activities that form part of their domestic responsibilities. In most Nigerian rural communities, women are primarily responsible for managing domestic affairs; this could range from cooking meals, cleaning the house and surroundings, caring for children and the elderly, gathering of firewood and wild food harvesting (Wuyep et al., 2014). While carrying out these activities

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under different capacities (housewives, traders, farmers), these women are said to have a close interaction with their environment and engage in various practices that are sustaining and protective of the environment (Wane and Chandler, 2002). Studies have also shown that women's traditional knowledge has helped them manage their environment for generations (Glazebrook, 2011); however, their contributions are rarely recognized because activities like cleaning and weeding are considered part of their responsibilities on the domestic front. This study aims to highlight rural women's contribution in environmental protection by examining how women in Makarfi Local Government Area (LGA) of Kaduna State, Nigeria, interact with their environment in different forms and how such interactions may contribute in protecting the environment. Sixty women shared their experiences and knowledge about the environment and how their traditional knowledge has helped them manage their interactions with the environment in a respectful and sustainable manner. This study did not only highlight the contributions of women in conserving the environment, but it also brought to the fore front challenges that women face in carrying out those activities. This is an important aspect of the discussion because most studies tend to focus on the former. The choice of the study site is significant because the Northern part of Nigeria has been described by the World Bank as underdeveloped compared to the rest of the country, many people turn to the environment for food and livelihood (World Bank, 2015). This study would add to literature in the field by highlighting a region that is underrepresented in studies. The study can also provide insights that can potentially contribute to policies on women's land rights, access to forest resources and development of environmental preservation strategies.

Women as environmental custodians: A review

Women's interaction with the environment has been studied from different perspectives at various times in history, however, since the 1970's when the Ecofeminist movement highlighted the connection between the suppression and exploitation of women and the degradation and exploitation of the environment (Mies and Shiva, 1993), various groups, and regions have adopted the concept and applied it according to their realities. In Africa, where women are said to have a close connection to their environment because of their reliance on it, arguments have been made about the experience that these women may have gathered in the areas of environmental conservation by virtue of their constant and historical interaction with it. Studies have described this interaction in terms of women's participation in subsistence farming, their Indigenous farming knowledge and methods that contribute to environmental conservation, and other studies also examine women's engagement in their daily activities that constitute efforts towards conservation. In a study on Gender, Knowledge and Practice in the formation and use of African Dark Earth (AfDE), it was found that women in Liberia and Sierra Leon, through their daily activities such as cooking and cleaning, add organic matter such as ash, potash and left over food and stalk onto the soil to form African Dark Earth (Frausin et al., 2014). This soil enrichment method which is solely based on traditional knowledge is said to improve soil quality as evident in the better crop yield from that soil in comparison to other fields. Although it is argued that women's reliance on the environment can sometimes be harmful to natural resources (Nankhuni and Findeis, 2004), this study shows that it can also be beneficial. However, there is need for more research and strategic planning to take into consideration factors such as poverty and cultural gender biases when mapping out conservation policies. The knowledge that most rural women in Africa rely on is largely based on traditions that have been passed down through many generations, it is therefore important to preserve such knowledge for future generations and women have an important role to play in this aspect. To emphasize the importance of traditional knowledge preservation, Debwa and Mearns (2012), highlighted the role of women, especially elderly women in preserving the knowledge of Indigenous vegetable production in Mantianeni, South-Africa. Young people in the community were showing little interest in the tradition and that raised concerns around sustainable production practices in the future. Elderly women in that community are looked up to as knowledge keepers, and therefore the responsibility of passing the knowledge lies on them. Through years of interaction with the environment, the older women have acquired knowledge that is crucial to maintaining the sustainable production of Indigenous vegetables in Mantianeni (Debwa and Mearns, 2012). Study has also shown that women's efforts towards protecting their environment can manifest through traditional practices such as crop rotation, mixed cropping and selective planting. Glazbrook (2011) noted that women in Ghana use these techniques in food production and to help them cope with climate change effect without exerting more damage to their environment (Glazbrook, 2011). In Nigeria, women in rural communities play a major role in the agriculture sector. They engage in the production, processing and marketing of food crops and they are said to contribute between 60 and 90% of the total agricultural production task in their various communities (FAO, 2011). This makes them engage significantly with their environment. Studies have shown that contrary to popular opinion, rural women do not only take from the environment, but they also give back. In Plateau state, north central Nigeria, women contribute in environmental protection through activities such as environmental sanitation, tree planting and traditional farming methods like mulching to conserve soil moisture (Wuyep et al., 2014). In the south western part of the country, women in Pedro Village, Lagos state were found to be protective and conscious of their environment. They manifest this by engaging in waste management, drainage management, water resource management, flood management and subsistence agriculture; these are all efforts towards protecting their environment (Chukwu, 2014). As a coastal community, they often experience flooding and that could be further exacerbated by blocked drainages and improper waste disposal. The study by Chukwu (2014) shows that women play an active role in protecting their community and serve as enforcers of guidelines and penalties.

Most rural dwellers in Nigeria depend on firewood as their primary source of cooking energy (Federal Ministry of Environment- FME, 2006), largely due to the lack of affordable alternatives and since women (especially women in rural communities) are mostly responsibility for cooking and gathering firewood, they are seen as significant users of this resource (Blackden and Quentim, 2006). While the level of tree harvesting by rural dwellers in Nigeria is said to be significant- 80% (FME, 2006), it is important to highlight the various roles women play in giving back to the environment and not to lose sight on areas of growth. This is why this study highlights both challenges and potentials; this would potentially give a more holistic picture of the issue and provide information for a more comprehensive policy formulation.

Description of study community

Makarfi LGA is located in the northern part of Kaduna states on latitude 11°2[1]N and longitude 7°40[1] E. It is bounded by Rogo LGA of Kano State at the northwest, Ikara LGA to the east, Kudan LGA in southwest and Sabon Gari LGA in the Southeast, it consist of ten wards with an aerial coverage of 650 km^2 (Umar et al, 2009) (Figure 1). It is located on a gentle undulating plain which extends almost unbroken from Sokoto down to Tuguddi near Agades in Niger Republic. Data shows that between 2006 and 2011, Makarfi's population was expected to grow from 146,574 to 170, 574 (National Population Commission of Nigeria, 2010). The growing population has led to increased demand for farm lands; the many years of interference with its natural environment has led to a derived vegetation cover at present. Presently, its vegetation cover consist of *Isoberlina, Dorka' isoberlina, tmentosa*, and *Uapca Fogemis* with a well-developed grass layer of *Tufted Andropenea*.

The study area is characterized by wet and dry seasons. The dry season begins in November and ends at May, and then the wet season begins with the little showers of rain leading up to its peak in August. It's marked with high temperature with major maximum of 40°C in April but a low atmospheric humidity (15 to 65%). The soil in the area consist of "fadama soils" comprising of vertisal's and clay (hydro-morphic), which promotes dry season farming of crops such as rice, sugar cane, and vegetables of various kinds. The upland soils promote the cultivation of crops like guinea corn, millets, soya beans, beans and groundnut (Kaduna State Government Development Strategies on Fadama II, 2002). Due to the favorable environmental conditions that support the growth of many crop varieties, farming has for many years been a major source of livelihood in the community (Strahler and Strahler, 2005).

DATA COLLECTION METHODS

This paper is based on a study conducted in Makarfi LGA October-November, 2016. In order to get a fair representation, six women were randomly selected from each of the following ten wards in Makarfi: Dandamisa, Danguzuri, Gazara, Gimi, Gubuchi, Gwanki, Makarfi, Mayare, Nasarawa Doya and Tudun Wada, respectively. A total of sixty women, between the ages of twenty to sixty years participated in the study. A semi-structured interview was conducted for each of the participants. These women shared their experiences from various perspectives, based on the roles and responsibilities they take up in their households and community. Since the study was aimed at highlighting women's role in environmental conservation, this age group (20-60) was ideal because women within this group in the community are mostly responsible for activities such as domestic work, farming and harvesting (Ekpo, 2012). This selection also provides an opportunity for generational knowledge perspective.

RESULTS AND DISCUSSION

Based on data collected, thirty women (50%) reported their occupation as farmers, while twenty four (40%) regard themselves as traders. The remaining six women reported occupations such as housewife (3%), and public servant (7%) respectively. As to the question of whether their various occupations make them interact with their environment, majority of the women (83%) agreed that as a result of their activities as farmers, traders or housewives, they are in constant contact with their environment. Women who engage significantly in farming activities in the community participate in various stages of farming. Women are involved in farm clearing, they engage in planting and weeding and they also participate actively in the harvesting and the sale of food. The seven percent of participants that reported as being public servants also said they engage in some kind of gardening, therefore they get some of their food from their gardens and through purchase as well. This goes to show that regardless of the occupation, all of the participants engage with the environment at various levels and degrees.

As part of their farming activities, women in Makarfi apply organic matter such as livestock waste, leftover food and ash to help enhance crop growth. These

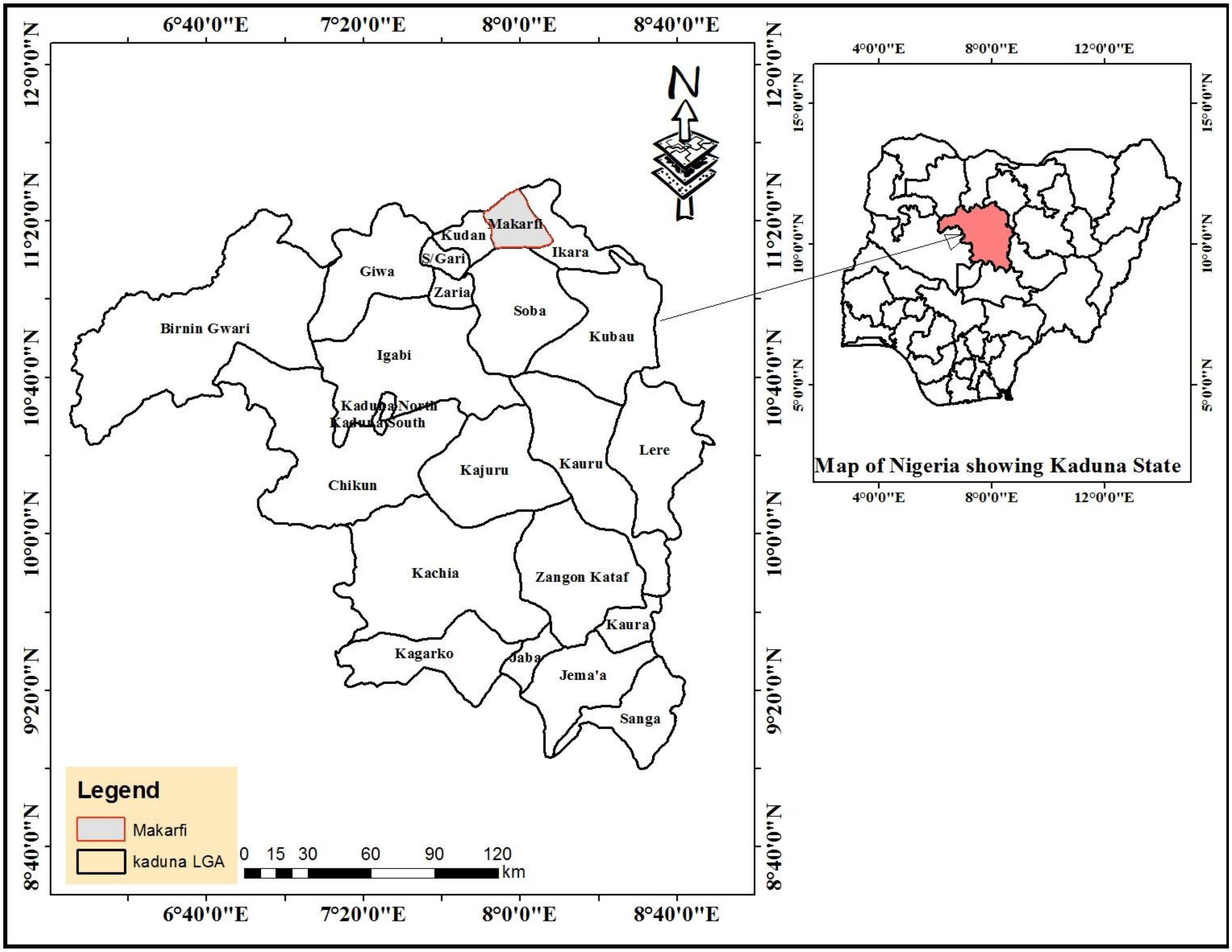

Figure 1. Map of Kaduna State showing Makarfi local government area. Source: Administrative map of Kaduna State.

procedures are said to also help enhance soil nutrients (Chukwu, 2014). Some women also engage in tree planting, although this activity is practised to a lower degree compared to the former (sustainable farming practises) as only seven percent of women admitted to planting at least a tree in the past year. Another form of environmental protection activity that women from the study area engage in involves sprinkling water on the soil before sweeping. This, the women say protects top soil, which in turn helps cub surface erosion. Thirteen percent (13%) of participants said they engage in sustainable harvesting so that those plants would be available for next time. One participant said:

“I remember been taught by my mother to carefully harvest spinach leaves to allow new leaves to grow back” (participant 50. Field interview, October, 2016).

Fire wood is the primary source of energy in the community and participants of this study admitted to utilizing fire wood as the first energy source for cooking. This is largely due to its accessibility and affordability. This is significant because ninety four percent (94%) of the participants fall under the income bracket of ten to twenty thousand naira ($32-$63) per month, so affording an alternate source of energy would come as a challenge to most of them (Chukwu, 2014). Some women also engage in tree an alternate source of energy would come as a challenge to most of them. However, they also admitted to cutting tree branches in ways that would allow for future germination of such tree. Furthermore forty six women (77%) said they gain up to eighty percent

Table 1. Summary of Participants Responses.

Occupation	Farmers	Traders	House wives	Public servants
No. of participants	30	24	2	4
Level/source of Income	10,000-20,000 Naira/month	< 10,000 Naira/month	>50% of income generated from farm related activities	< 50% of income generated from non-farm related activities
No. of participants	56	4	46	14
Level of Interaction with the environment	High (5-7 times/week)	Moderate (3-5 times/week)	Low (2- 3 times/week)	Very low (<2 times/week)
No. of participants	50	10	-	-
Environmental protection practices	Tree planting (in the past 12 months prior to the study)	Sustainable farming practices (e.g. use of livestock waste, leftover food as manure)	Sustainable harvesting (e.g. harvesting matured plants to enable young ones regenerate)	Sprinkling of water before sweeping top soil to prevent erosion
No. of participants	4	60	60	60
Challenges to environmental protection efforts	Poverty	Cultural practices restricting women's access to land	Lack of government support- tree planting initiatives	Lack of access to alternative sources of cooking energy

(80%) of their income through activities such as farming, sale of farm produce, sale of firewood and wild food. These activities happen in close relation with the environment, which speaks to why they would be concerned with the health of their environment.

In their quest to protect their environment, these women reported facing challenges of various kinds. Of the sixty women that participated in the study, forty five percent (45%) of them said they are enthusiastic about protecting the environment; however they are limited by their state of economic well being. These women recognize that activities such as tree felling and excessive use of farmlands for crop production sometimes bring negative effects to the environment, but they lack the resources to move to other sources of energy in order to reduce dependence on trees for firewood. Some twenty five percent (25%) of the women reported having challenges with cultural practises that restrict women's access to land. Because of limited resources women are often not able to purchase land or access credit to acquire land. Cultural practises that discriminate against women inheriting landed properties also pose a barrier to land acquisition. This challenge cuts across many rural communities in Nigeria where women's access to land is largely done through male relation (Simpa, 2014). Because of limited access, these women cannot easily move from one farmland to another, to limit overuse of certain spaces. Even with the best of intentions for the environment, a woman would want to look after her family by making sure she farms on available land. This is why twenty percent of the women say that the government has a role to play in the conversation. The women said that the government can assist by providing affordable energy sources, more tree planting initiatives to make up for trees lost resulting from human activities. Table 1 summarizes the results.

Conclusion

This study has shown how women, through their various occupations as farmers, housewives, traders and public servants have close relations with the environment and relies on it for food and income. Because of how significant the environment is to their livelihood, women in Makarfi carry out various practices to help protect the environment. This include sustainable farming practices (like the use of organic matters such as livestock waste and left over food to enhance crop production), tree planting, sustainable harvesting (harvesting matured plants to enable young plants to regenerate) and practices to reduce soil erosion (like sprinkling of water on the ground before sweeping). This study has also highlighted challenges that women face in their quest to protect the environment; they range from poverty, to challenges with cultural practises and the lack of government assistance. Since women in rural Nigeria contribute significantly to agricultural labour (IFAD, 2012), and are mostly responsible for managing their household chores (like sourcing for cooking fuel, cleaning their surrounding, and waste management), it is only logical that policies reflect the important position of these women. However, rural women and women headed households in the county's rural communities remain among the poorest in their communities (Oluwatayo, 2014). Until there is a sincere commitment by policy makers to empower rural women and recognize them for the important role they play, a healthy natural environment with reduced threat to resources such as trees may be extremely difficult to achieve in Nigeria without the commitment and input from a group (rural women) who have close interaction with the environment. Many participants of this study discussed their willingness and desire to do more to make sure the environment that provides for their needs today will still be there for their children in the future. With support, these desires can be fulfilled. The environmental protection practices already used by women in Makarfi are based on traditional knowledge, however they can make use of more training on other innovative techniques that would complement their traditional knowledge to help them better protect their environment. Due to their frequent interaction with the environment, these women can potentially form part of natural disaster management programmes and climate change adaptation programmes. Customary laws should better protect women's rights and access to resources such as land. This would help women get more access to incentives such as loans, which will in turn help empower them to choose more environmental friendly options like using an alternative source of energy instead of cutting down trees, or using more organic options during crop production. The importance of women's participation in environmental protection has been reiterated by the United Nation (UN, 2002). When rural women are seen as partners in policy decision forums, then their contributions and traditional knowledge will begin to be recognized and appreciated. Their contributions can serve as foundations that can potentially be built upon towards sustainable rural development.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Full Length Research Paper

Physicochemical properties of soils and some water sources on the Eastern Flank of Mount Cameroon

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Human activities such as agriculture, construction of houses and automobile workshops and natural processes alter the properties of soils and water which affect the health of plants, animals and humans. This work was therefore, aimed at investigating some physicochemical properties of soils and some water sources on the Eastern Flank of Mount Cameroon with altitude and selected natural and/or anthropogenic activities. Soils and water were sampled in February 2010 and analysed for their physicochemical properties using standard methods. The results of the soil analysis showed that all the soils in the region were acidic. Most of the physicochemical properties of the water analysed were within acceptable limits of WHO. The water sources between Tiko and Wonya-Mavio, Buea had higher nitrate. There were significant positive relationships ($p < 0.05$ and $p < 0.01$) between nitrogen and altitude and carbon and altitude, respectively. Magnesium and ECEC showed a significant negative correlation ($p < 0.05$) with altitude while calcium showed a highly significant negative correlation with altitude. Natural sources of pollution identified are weathering, erosion and sea water intrusions. The anthropogenic ones include wastes from homes, laundry, fertilizers and factories. Stringent soil and water management scheme or legislature is recommended.

Key words: Soils, physicochemical properties, Mount Cameroon, pollution, water, human activities, fertilizers.

INTRODUCTION

Soil is the dynamic link between the biosphere and lithosphere and constitutes a practically not renewable (very low rate of formation) natural resource, with a key role for the environment and for agriculture (Moraetis et al., 2016). Some factors such as altitude, parent rocks, vegetation and anthropogenic activities influence the physicochemical properties of soil and water like pH, organic matter, CEC, soil texture and water chemistry.The soil is composed of air, water, inorganic and organic matter in varying proportions. Its physicochemical properties such as texture, organic carbon, cation exchange capacity (CEC) and pH are determined by the

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percent composition of the above parameters (Wild, 1996). Soil pH affects nutrients availability and the optimal condition for this is at pH 5 to 7 (Arp and Krausse, 2006).

Soil texture affects drainage, water and nutrients storage and the optimal conditions for this are sandy loam, loam and silt loam soils (Arp and Krausse, 2006). A research conducted in Australia on comparing the chemical properties of a long term cultivated site to those of an uncropped and highly grazed reference site in a red brown earth soil showed that the total carbon decreased from 3.74% on the grazed site to 1.66% on the cultivated site. This was attributed to the fact that cultivated soil was more prone to surface sealing and erosion processes than the grazed soil (Whitbread et al., 1998).

In another study, it was observed that the rate of change in bulk density decreased with depth. For entire soil profile (0-horizon to 40 cm) the rate of carbon accrual was 1.5% per year. Nitrogen (N) stocks were affected by disturbance in the 0-horizon. Nitrogen accumulated at 0.6% for the entire soil profile (Maloney, 2008).

The soil plays a great role in the environment which can be seen in chemical and physicochemical adsorption, agricultural and pollutant retention. The chemical and physical properties of soils are controlled largely by clay and humus. They are the centres of activity around which chemical reactions and nutrient exchanges occur. Furthermore, by attracting ions to their surfaces, they temporarily protect essential nutrients from leaching and then release them slowly for plant use (Brady, 1984).

Soil productivity is dependent on the ability of the soil to provide water, nutrients and oxygen to plant root system as well as limiting exposure of the root system to toxic gases or solutions (Schumacher, 2006). Tillage erosion causes reduction in effective rooting depth, plant nutrients; available plant water soil organic matter and land area (Schumacher, 2006). Bush fire destroys vegetation and leaves the soil bare, loose and susceptible to erosion. Every year acid rain causes hundreds of millions of dollars' worth damage to storey buildings and statutes throughout the world (Chang, 2005).

Some activities often lead to the destruction or contamination of the environment. The natural activities include contaminated rain water (e.g. acid rain which results from emission of acidic gases into the air), winds, volcanic eruptions and forest fires. The anthropogenic activities come from industries (paper, automobile, and oil industries), homes (household wastes, paints and pesticides) and agriculture (e.g. fertilizers). Farming and grazing involve the use of fertilizers which is source of pollution (Asongwe et al., 2016).

Uncontaminated rain water is naturally acidic and generally has a pH of about 5.6. Generally acid rain is derived from SO_x and NO_x. Acid rain is, however, more acidic than normal rain water and typically has a pH value of about 4 (Brown et al., 2003). Acid rain is also toxic to vegetation and aquatic life. Many well-documented cases show dramatically how acid rain has destroyed agricultural forest land and killed aquatic organisms (Chang, 2005). In the North-Eastern United states and adjacent part of Canada, acid rain has killed fish, decimated forests, injured crops and released harmful substances into the soil (Silberberg, 2000).

Humans, animals and precipitation (runoff) are the principal agents (mechanisms) of contaminant transport (Folefac et al., 2009). There are a wide number of water bodies along the mount Cameroon region. Some of these are streams, wells and rivers. Groundwater is the only reliable water resource for drinking, domestic, and agricultural purposes for the people living in the Mount Cameroon area (Ako et al., 2012). Runoffs into these water bodies often carry or contain chemical substances which could be dangerous at high concentrations. The inhabitants use these water bodies for various purposes such as bathing, cooking washing of clothes or cars etc. The probability that they are often contaminated from wastes dumped into them and from the human activities that take place around them could therefore be high.

Water is used in homes for various activities, in industries and to give support to aquatic life and the mangroves. Despite the fact that there are many natural or fresh water sources in the country, water management and challenges are enormous. Numerous studies within Cameroon portray that most water resources used for domestic consumption are polluted (Asongwe, 2010; Forton et al., 2012).

We need good, clean potable water for good health. There has been increasing indiscriminate disposal of domestic, industrial and agricultural wastes on soil and water that exposes them to pollution. Water pollution is therefore an area of great concern. This work is therefore, aimed at investigating the physicochemical properties of soils and some water sources within the Eastern flank of Mount Cameroon relating them to natural and/or anthropogenic activities within this sub-region. It is also also aimed at comparing properties of uncultivated (for at least two years) soil to those of cultivated soil and variation with altitude and make recommendations.

MATERIALS AND METHODS

Description of site

The area under study is the West slope of Mount Cameroon, in Fako Division of the South West Region of Cameroon. It spans from Limbe down beach and Mile 4 through Mutengene, Tiko including Mile 14 Dibanda, Mile 16 Bolifamba, Mile 18 Molyko, Bomduma, Bokwango to Vasingi in Buea Sub-Division. It lies between longitudes 8° 5' E and 9° 32'E and latitudes 3° 50'N and 4° 22' N (Figures 1 and 2).

The region is composed mainly of volcanic rocks which range from massive basaltic lava flows around the upper slopes of Mt. Cameroon to pyroclastic materials further down slope (Endeley et al., 2001; Manga et al., 2013). The soils have been weathered and partly covered by more recent deposits; hence the soils are mostly

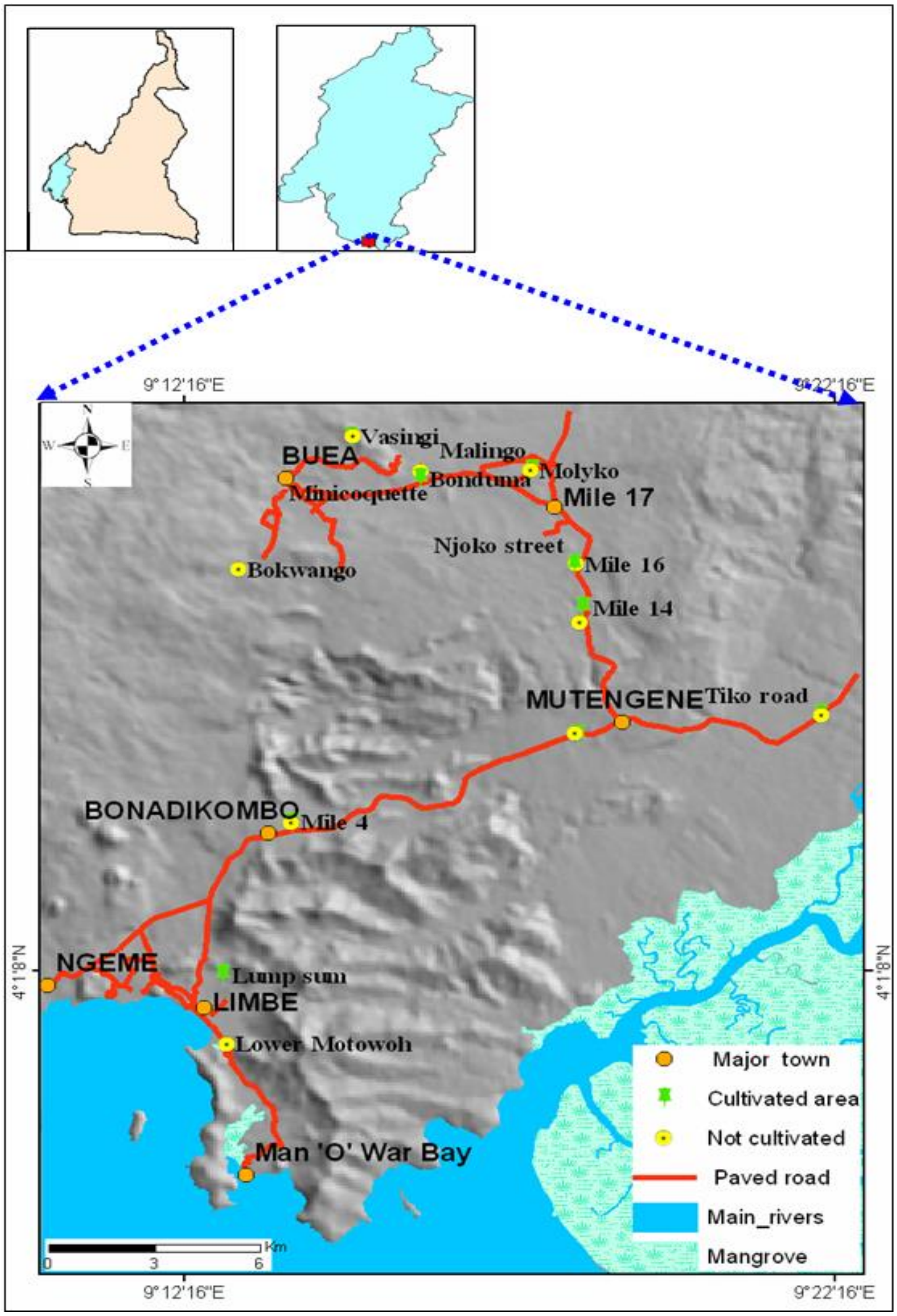

Figure 1. Map of the study area showing sample points (Drawn from GPS data by Che Vivian, PhD. Department of Geology, University of Buea).

black and are well drained due to the generally hilly nature of the terrain. Climatic conditions such as temperature (20 to 28°C), and annual rainfall (3000 to 5000 mm) (Manga et al., 2013) are favourable for agriculture. The geochemistry of volcanic rocks from the entire CVL shows that the rocks all have MgO > 4% and are relatively rich in trace elements (Fitton and Dunlop, 1985). The area has many hills, gulley, streams as well as underground water. It is prone to many natural hazards, such as floods and eruptions. The population is cosmopolitan with most of the people living on small scale or peasant farming. Most of the land is occupied by the Cameroon Development Corporation (CDC) for Banana, Palm and Rubber plantations. Limbe has a lot of industrial activities such as petroleum, fishing, agriculture, photography etc. A lot of construction work is going on especially in Buea to cater for the increasing population especially the University of Buea students and staff (Figures 1 and 2).

The likely sources of pollution would be the volcanic rocks and sea intrusions (Natural) and activities such indiscriminate dumping

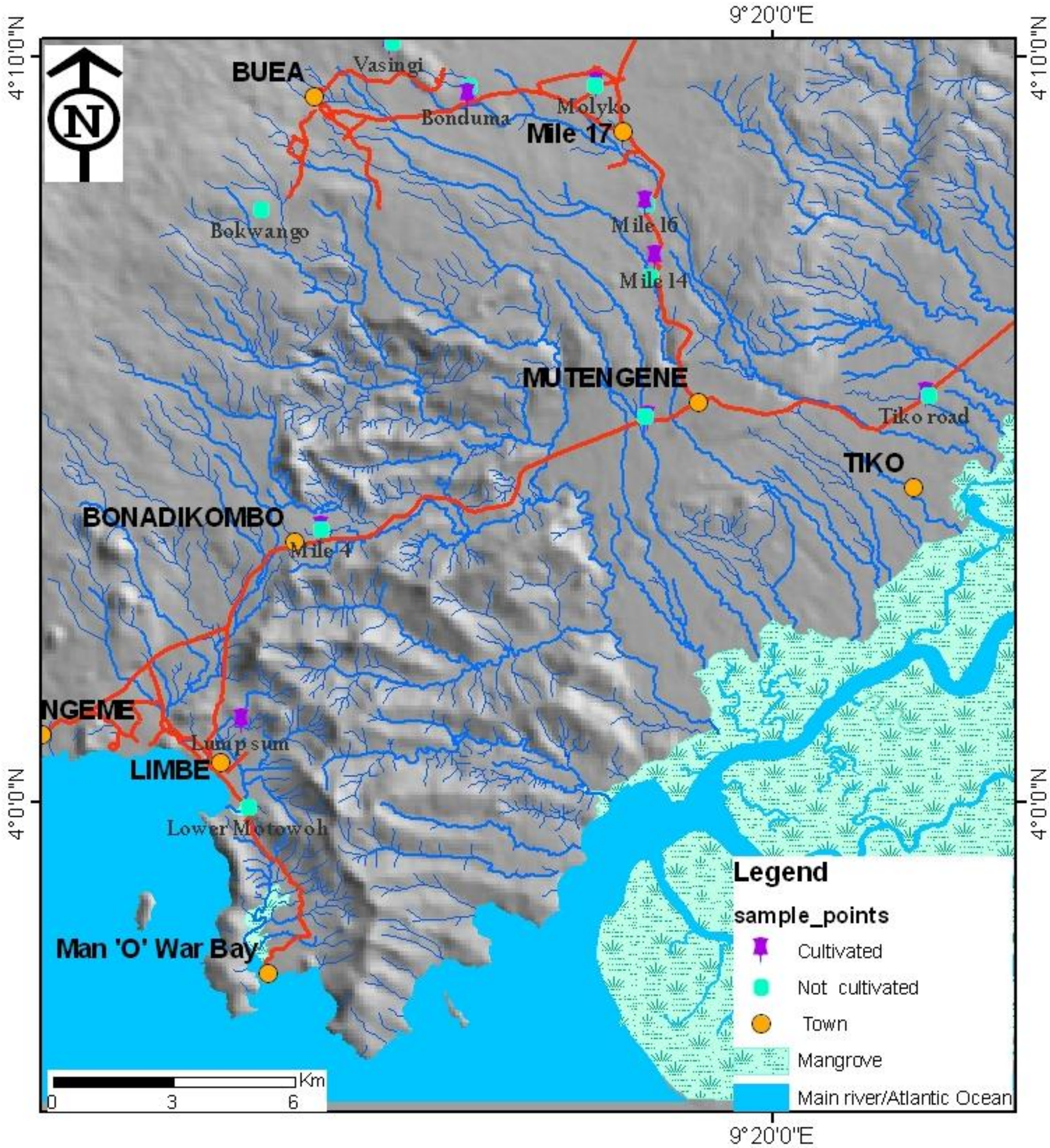

Figure 2. Hydrological map of the study area (Drawn from GPS data by Che Vivian, PhD. Department of Geology, University of Buea).

of waste, laundry, use of chemicals in farms and industries, location of latrines etc (anthropogenic).

Sampling of soils

Top soil samples were collected using a hand trowel from cultivated and abandoned (Non-cultivated) areas at the range of 15 to 20 cm depth. The points were chosen at different altitudes such that a cultivated point had a corresponding non-cultivated point a few metres away from each other. At each collection point, four soil samples were collected at about 1 m apart and bulked. The sampling points were geo-referenced using a 12-channel Garmin etrex Global Positioning System (GPS) (Table 1).

Water sampling

Some common water sources of each locality were chosen. Water was collected into 1.5L containers. Table 2 gives the sampling stations for water samples, source of water and their locations. Main water types in the study area are Ca-Mg-HCO($_3$) and Na-HCO($_3$). Three processes control the spring water quality. CO($_2$)-driven silicate weathering and reverse cation exchange are the most important processes affecting the hydrochemistry of the spring waters. While tropical oceanic monsoon chloride-rich/sulfate-rich

Table 1. The sampling stations for soil samples, their location, altitude, GPS location and Human activities around them.

Sampling station	Location	Altitude (m)	GPS location	Human activity
1 (NC)*	Lower Motowo Down Beach	4.27	N 03° 59.904′; E 009° 12.950′	Fishing and sales of sea products
2 (C)	Tita Street Beach	31.39	N 04° 01.0141′; E 009° 12.872′	Farming, domestic waste dump, use of fertilisers
3 (C)	Mile 4	231.65	N 04° 03.650′; E 009o 13.931′	Farming, Domestic waste dump, use of fertilisers
4 (NC)	Mile 4	224.94	N 04° 03.698′; E 009° 13.934′	Palm plantation
5 (C)	Limbe Road Mutengene	194.46	N 04° 05.132′; E 009° 18.335′	Farming, construction of buildings
6 (NC)	Limbe Road Mutengene	177.39	N 04° 05.159′; E 009° 18.297′	Palm plantation
7 (C)	Douala Road, Tiko	46.33	N 04° 05.458;′ E 009° 22.067′	Farming
8 (NC)	Douala Road Tiko	28.65	N 04° 05.457′; E 009° 22.090′	Rubber plantation
9 (NC)	Mile 14	381.61	N 04° 07.044; E 009° 18.370′	Abandoned for long
10 (C)	Mile 14	412.09	N 04° 07.279′; E 009° 18.412′	Farming, domestic waste dump, use of fertilizers.
11 (NC)	Mile 16	484.63	N 04° 08.026′; E 009° 18.311′	Construction of houses, domestic waste dump
12 (C)	Mile 16	462.08	N 04° 08.013′; E 009° 18.279′	Farming, construction of houses, fertilizers
13 (C)	Malingo Street Molyko	465.43	N 04° 09.609′; E 009° 17.638′	Farming, intense construction of houses
14 (NC)	Malingo Street Molyko	563.88	N 04° 09.590′; E 009° 17.617′	Construction of houses
15 (NC)	Mini Coquette Bondoma	699.21	N 04° 09.469′; E 009° 15.930′	Abandoned
16 (C)	Mini Coquette Bouduma	688.54	N 04° 09.465′; E 009° 15.903′	Farming, construction of houses
17 (NC)	Bokwango Towards Sasse	945.18	N 04° 07.943′; E 009° 13.150′	Domestic waste dump, abandoned
18 (C)	Bokwango Towards Sasse	945.79	N 04° 07.936; E 009° 13.132′	Farming, domestic waste dump
19 (C)	Vasingi	1017.12	N 04° 10.182′; E 009° 14.848′	Farming, domestic waste dump
20 (NC)	Vasingi	997.31	N 04° 10.192′; E 009° 14.883′	Domestic waste dump

*C, Cultivated; NC, Not cultivated for at least two years.

rainwater seems to affect spring water chemistry at low-altitude areas (Ako et al., 2012). Figures 3 and 4 also show some of the water sampling points.

Soil analytical methods

Various methods were used to analyse the soils for their physicochemical properties.

Particle size analysis

Particle size analysis was done by sedimentation and decantation method (Akinola, 1986). To 50 g of dry sample in a 250 ml beaker was added distilled water above the soil to soak. 20 ml of 0.5 N sodium hexametaphosphate $(NaPO_4)_6$ was added to the mixture and allowed to stand for 15 minutes. A magnetic stirrer and bar was used to stir the mixture for five minutes. The content of the beaker was transferred into a 1-L measuring cylinder and water added to the 1 L mark. Using one palm of the hand to cover the mouth of the cylinder and the other palm to hold its bottom, the contents of the cylinder were shaken several times and then allowed to stand for two hours.

After two hours, the suspension was decanted using a tube. The sand and silt sediments were transferred into a beaker, rinsing the measuring cylinder with distilled water, using a wash bottle. It was allowed to stand for 30 min to an hour and a second decantation was done. The sand and silt was dried on a giant hot plate for about 12 h, stirring until the sticky nature was absent. The beaker, sand and silt were weighed. Water was added into the beaker containing sand and silt and allowed to soak, stirring and washing with hand several times, decanting until the water above the sand was very clear. The sand was dried in the oven and then weighed after cooling.

Chemical analysis

Soil pH was measured in 1:2 soils: water suspension as well as in soil: KCl suspension using a PHS-2CW Microprocessor pH/mV glass - electrode meter.

Organic carbon was determined in the Walkley-Black

Table 2. Sampling stations, location and altitude for water sources.

S/N	Source	Location	Altitude (m)	Remarks
1	Well	Beach Limbe	4.27	Not covered, used for domestic activities
2	Stream	Beach Limbe	4.27	Running stream, dirty.
3	Stream	Mile 4 Limbe	231.65	Running stream used for domestic activities
4	Spring	Mutengene	194.46	Used for domestic activities
5	Well	Douala Road Tiko	46.33	Covered, used for domestic purposes
6	Stream	Ndongo Tiko	46.33	Dominance of vegetation
7	Stream	Benyo (Mile 14)	412.09	Agricultural activities, used for laundry and equally for domestic activities.
8	Stream	Washing point Mile 16	484.63	Washing of vehicles
9	Spring	Mile 18	462.08	Used for domestic activities
10	Well	Wonya Mavio	563.88	Covered, used for domestic activities and gardens around it.
11	Spring	Bonduma	699.21	Dominance of vegetation, used for domestic activities
12	Stream	Ndongo Molyko	688.54	Disposal of waste , used for laundry, some domestic and irrigation
13	Stream	Ndongo Likomba	70.64	Used for laundry, Waste disposal
14	Stream	Ndongo Mile 16	462.08	Waste disposal
15	Spring	Vasingi	997.31	Used for domestic activities
16	Spring	Mile 4 Limbe	231.65	Used for domestic activities

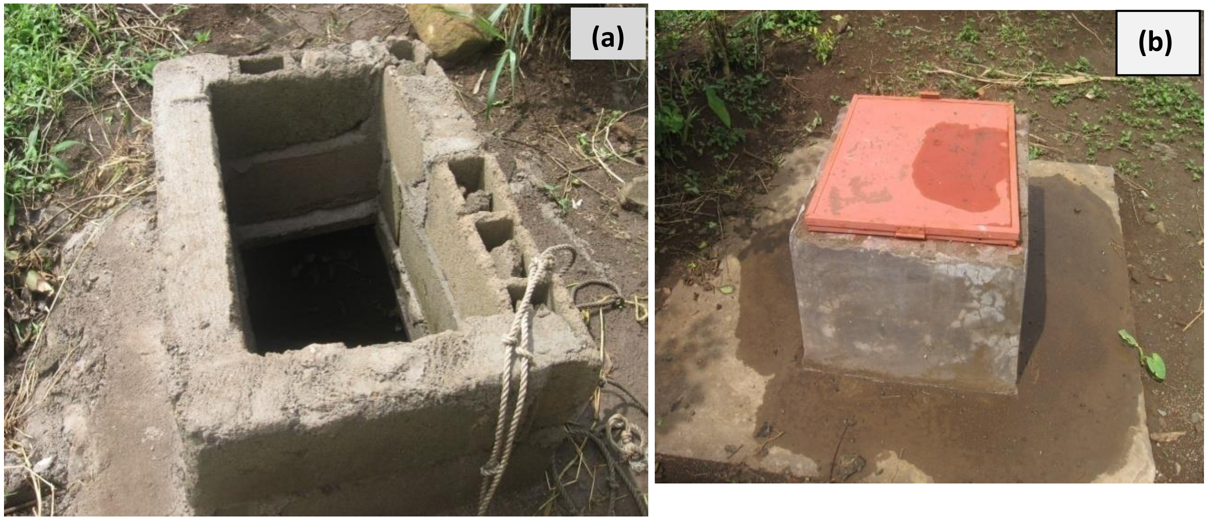

Figure 3. Open (a) and closed wells (b) at Wonya-Mavio, mile 18 Buea.

Figure 4. Springs at Mercedes street, (a) Bonduma and (b) Mile 18, Wonya- Mavio, Buea.

dichromate titration method following digestion with potassium dichromate and concentrated sulphuric acid (Walkley, 1987). The concentration of the green chromium obtained after oxidation is determined by colorimetry. A factor F=mg C/OD was calculated for each standard, an average calculated and % carbon calculated from % C= OD sample × 1.33/5.

Total nitrogen was determined by modified macro-Kjeldahl method (Jackson, 1958). Soil was digested at 370°C on a Digestion System 40 1016 Digester with concentrated sulphuric acid in the presence of sodium sulphate-Selenium catalyst. The digest was diluted and the nitrogen as $(NH_4)_2SO_4$ was determined by colorimetry.

Available phosphorus was extracted with Bray-P-1 solution and the colour was developed using Murphy and Riley reagent, and ascorbic acid. A solution of 0.1 NHCl and 0.03 N NH_4F was used to extract available phosphorus from the soil. Phosphorus was determined by colorimetry using ammonium molybdate and ascorbic acid. Available phosphorus was read at a wavelength of 882 nm (Bray et al., 1945). Exchangeable potassium was extracted with 1 N NH_4OAC (pH 7) and was determined using a Gallenkamp Digital Flame Analyser.

Water analytical methods

Various methods were used to analyse the physicochemical properties of the different water sources.

Bicarbonate (HCO_3^-)

The concentration of bicarbonate (HCO_3^-) was determined by titration. For each sample, 50 mL was transferred into a 250 ml conical flask pipette. Four drops of methyl red indicator was put in sample and titrated with 0.01 N HCl from burette and the volume of the acid titrated and the end-point recorded where a steady colour changed to orange was observed.

The concentration of HCO_3^-:

$$\text{mg/L} = \frac{(Y\text{-}X)\ \text{mL} \times .01 \times 103}{V\ (50\ \text{mL})}$$

Y = initial volume of acid; X = final volume at end-point; V = volume transferred

$$HCO_3^-{}_{(aq)} + H^+{}_{(aq)} \longrightarrow CO_{2(g)} + H_2O_{(l)}$$

Chloride (Cl^-)

Chloride (Cl^-) ion concentration determination was carried by titration. One hundred millilitres of sample was transferred into a 250 ml conical flask using a pipette. Four drops of K_2CrO_4 indicator added to the sample with small quantity of $CaCO_3$. $AgNO_3$ solution titrated drop wise from the burette until solution turns a permanent orange tinge colour. The volume of the $AgNO_3$ was added until an end-point (end-point = point where a permanent orange tinge colour) was observed. A blank titration was also performed with distilled water and the volume subtracted from the samples. The chloride concentration was gotten as follows:

(Sample titration - blank titration) × 10 = mg/L of Cl^- in the sample.

Magnesium (Mg^{2+})

Magnesium (Mg^{2+}) ion concentration was analysed using the colorimetric method. One millilitre of water samples and standards, 1.25 ppm $Mg^{2+}{}_{(aq)}$ (prepared from magnesium ribbon, dilute HCl and 25 ml of 1 N ammonium acetate) were pipetted into clean test tubes. Four millilitres of calcium chloride solution and 10 ml of titan yellow mixture added immediately. 2 ml of alkali mixture was then added and was vigorously shaken on the electric homogenizer for 60 min for colour development and read on a spectrophotometer.

Nitrate (NO_3^-)-nitrogen (N)

For NO_3^--N determination, the colorimetric method was used. Five millilitres of standard and water samples were pipetted into clean test tubes. One millilitre salicylic acid (5 g dissolved in 1 L concentrated H_2SO_4) solution was added to each test tube, immediately mixed well and left for 30 min. Ten millilitres of 4 M sodium hydroxide was then added to each tube and left for one hour for full colour development. The colour was stable for 12 h and absorbance read at 410 nm wavelength on an SP-300 spectrophotometer. A factor F, for the standards was calculated and the average Fav used to calculate the NO_3^--N as:

% NO_3^--N= 0.0004 × Fav × (Abs-blank)

Sulphate (SO_4^{2-})

Sulphate (SO_4^{2-}) ion was analysed by turbidimetry with 10 mL of standard solutions of sulphates (0.543 g of K_2SO_4 + 68 mL of 25% HCl all in 1000 mL distilled water) and water samples pipetted into test tube. Two millilitres of 25 mL standard solution was added to samples and standards. One millilitre of the turbidimetric reagent (gelatine/$BaCl_2$) was added and finally made to 15 mL with distilled water. The contents were then shaken and allowed to stand for about 20 min and absorbance measured at 450 nm wavelength on an SP-300 Spectrophotometer.

Phosphate (PO_4^{3-})

Phosphate (PO_4^{3-}) ion was determined by colorimetry (using ammonium molybdate-ascobic acid blue coloration method). Five millilitres of water sample and standard solution (prepared by dissolving 0.526 g of KH_2PO_4 in 50 mL extracting solution (0.1 NHCl +0.03 N NH_4F all to1000 mL with distilled water) were pipetted into clean test tubes. Five milliliters of mixed reagents (250 mL of 2.5 M Conc. sulphuric acid, 75 mL of 4% ammonium molybdate) was added to each test tube. 15 mL distilled water was added and stirred vigorously and kept for 15 min for colour development and absorbance read at 650 nm wavelength on the spectrophotometer. The Perkin-Elmer Spectrophotometer 295E was used for all the readings.

Sodium (Na^+) and potassium (K^+)

The concentrations of sodium (Na^+), potassium (K^+) were determined using the Gallenkamp Digital Flame Analyser. The principle of flame photometry is such that over certain concentration ranges, light emitted as electrons fall to their ground state after atomic excitation by flame, which is directly proportional to the concentration of the samples or standard (1.491 g KCl/L or 0.1169 g NaCl/L) being aspirated. The instrument translates the emitted photon to digits, which were read on the digital display on the meter.

Experimental data was analyzed with the statistical package SPSS14.0 and EXCEL 2007 for Windows. Correlation analyses were also done to establish the likely sources of pollutants.

RESULTS AND DISCUSSION

Physicochemical properties of soils

The results of the physicochemical properties of the soils from the study area are presented in Table 3. The results indicate that 60% of the soils in the region are loam while 40% are clay-loam. In 70% of the soils, the clay content ranged from 16 to 25%.This indicates that the clays are almost uniformly distributed in the soils of this area and might have been derived from basaltic rocks that dominate this region (Endeley et al., 2001).

The soil pH in water ranged from 5.60 to 6.71 which is adequate. The optimal range for availability of nutrients is 5 to 7 (Arp and Krasse, 2006). This implies fertilizer application is needed for maintenance. Soil pH plays an important role in the availability of nutrients. The different forms of some nutrient elements are greatly determined by the pH of the soil (Brady, 1984). Ngane et al. (2012) also observed low pH values in some soils from South-Eastern Cameroon.

Magnesium and calcium concentrations decreased with altitude (Figure 5). The highest values (35.84 mmol/100 g and 12.28 mmol/100 g for Ca and Mg, respectively) were recorded in Limbe Downbeach (4.27 metres above sea level) and the lowest values (7.09 mmol/100 g and 2.22 mmol/100g for Ca and Mg, respectively) were observed in Vasingi (997.3 m above sea level). Calcium had a significant negative correlation ($r = - 0.57$, $p < 0.01$) while magnesium had a significant negative correlation ($r = - 0.50$, $p < 0.05$) with altitude (Figure 6). These significant negative relationships between these properties of soils and altitude could be attributed to weathering of rocks at higher altitudes and transportation to lower altitudes.

The results of properties of soils from cultivated and uncultivated areas are presented in Tables 4 and 5, respectively. The mean value of organic carbon in the non-cultivated area was 2.89% while that of the cultivated areas was 2.62% showing a decrease in organic carbon on cultivation. In a similar research conducted in Australia; on comparing the chemical properties of a long term cultivated site to those of an uncropped and highly grazed reference site in a red brown earth soil, total carbon decreased from 3.74% on the grazed site to 1.66% on the cultivated site.The mean total nitrogen content in the non-cultivated areas was 0.32% while in the cultivated areas; it was 0.24% showing a decrease in total nitrogen content on cultivation. Again on cultivation; the mean ECEC decreased from 20.17 to17.85 mmol/100g representing 11.50% decrease in ECEC on cultivation. This implies the numbers of exchangeable sites are reduced on cultivation and contamination of water sources with cations shall increase. The mean available phosphorus decreased from 26.7 to 17 mg/kg. This represents a 36.33% decrease in available phosphorus on cultivation. Generally, there was a significant decrease in nutrients on cultivation or the properties of the cultivated areas were different from those of non-cultivated areas. Farmers may be tempted to increase fertility of the soils by fertilization. The inhabitants are advised not to cultivate around residential areas or around the water sources. In a similar study, Kizilkaya et al. (2010) found that land use change and subsequent tillage practices resulted in significant decreases in organic matter, total porosity, total nitrogen and soil aggregates stability.

From the correlation analysis of the soil properties (Table 6 and Figures 6 and 7), there were negative

Table 3. Physicochemical properties of soils from the study area

S/N	Moist content (%)	pH H_2O	pH KCl	Org. C (%)	Tot. N (%)	C/N	Avail. P (mg/kg)	Exchangeable bases Ca (mmol/100g)	Mg	K	Na	Exch. acidity	ECEC	BS	Sand (%)	Silt (%)	Clay (%)	Textural class*
1	14.87	6.15	5.09	1.92	0.21	9	65	35.84	12.28	0.64	0.07	0.29	49.12	99.41	36.4	40.6	23.0	L
2	16.82	5.93	4.77	1.54	0.11	14	1	19.41	6.40	0.33	0.04	0.34	26.52	98.72	33.0	29.8	37.2	C L
3	16.41	6.03	4.90	2.27	0.12	19	2	15.61	4.87	0.65	0.08	0.31	21.52	98.56	34.6	31.0	34.4	CL
4	17.32	5.83	4.80	2.78	0.18	15	11	10.04	3.02	0.39	0.06	0.43	13.94	96.92	46.0	31.1	22.9	L
5	9.64	6.23	5.21	1.98	0.26	8	45	17.00	5.89	0.82	0.11	0.25	24.07	98.96	47.7	35.7	16.6	L
6	13.59	6.22	5.04	2.45	0.26	9	51	17.52	5.84	1.59	0.15	0.26	25.36	98.98	46.2	35.4	18.4	L
7	12.26	6.26	4.99	1.87	0.12	16	23	14.09	4.69	0.37	0.08	0.20	19.43	98.97	35.5	40.6	23.9	L
8	14.50	5.84	4.42	1.67	0.11	15	4	13.68	4.31	0.90	0.07	0.42	19.38	97.83	29.7	42.2	28.1	CL
9	17.83	6.02	4.93	3.12	0.28	11	3	12.02	4.34	0.33	0.05	0.29	17.03	98.30	37.0	32.6	30.4	CL
10	17.60	6.24	5.18	3.12	0.28	11	5	11.51	3.74	0.82	0.06	0.11	16.24	99.32	32.2	30.6	37.2	CL
11	19.9	6.05	4.71	2.00	0.16	13	1	9.43	3.77	0.95	0.07	0.49	14.71	96.67	13.4	32.1	54.5	C
12	14.44	5.85	4.46	1.99	0.09	22	38	7.51	2.85	0.22	0.07	0.31	10.96	97.17	21.7	48.7	29.6	CL
13	21.99	5.60	4.46	2.45	0.48	5	29	8.35	3.32	0.68	0.13	0.87	13.35	93.48	32.4	43.7	23.9	L
14	19.01	6.01	4.47	2.07	0.54	4	34	11.28	3.42	1.27	0.12	0.51	16.60	96.93	38.1	41.0	20.9	L
15	13.42	6.71	5.30	3.72	0.54	7	35	13.65	4.53	1.99	0.19	0.33	20.69	94.41	38.7	46.3	15.0	L
16	12.42	6.09	4.78	3.22	0.24	6	12	7.09	2.59	0.37	0.05	0.44	10.54	95.83	31.1	49.8	19.1	L
17	20.48	6.18	5.08	6.30	0.71	9	53	8.65	2.87	1.07	0.12	0.57	13.28	95.71	28.5	42.0	29.5	CL
18	21.19	5.80	4.40	4.74	0.58	8	11	15.38	6.69	0.28	0.04	0.52	22.91	97.73	28.6	46.3	25.1	L
19	20.60	6.18	5.00	3.03	0.12	25	4	8.66	2.22	1.69	0.18	0.25	13.00	98.10	31.7	41.6	26.6	L
20	18.17	5.77	4.60	2.88	0.25	12	10	7.16	2.72	0.99	0.09	0.58	11.54	94.97	32.4	46.8	20.8	L

*L = loam, CL= clay loam, C = clay.

correlations between ECEC and Clay (r = -0.12) and ECEC and organic carbon (r = -0.26) which were insignificant ($p > 0.05$). The negative correlation between ECEC and clay could be an indication that the clays are mostly 1:1 clays or oxide and hydroxide clays, which have very little exchange sites for cations. The negative correlation between ECEC and organic matter could be an indication that the soils are made up of substances which are neither fulvic acid nor humic acid. This implies most of the soils could be young soils. Magnesium increased with calcium (Figure 7a). This implies both magnesium and calcium could have the same origin.

Organic carbon and clay constitute the absorption complex of soils. This implies that the exchangeable bases can be mobile through the clays and will not be trapped. Hence, they can find their way into drinking water sources in this region. This is dangerous. If the amounts of these bases have not yet reached threshold values this could be because the activities leading to their presence in soils are not yet very much. The highest exchange acidity was at Malingo Street, 0.87 mmol/100g. The highest concentration of Na^+ was at Bonduma, 0.19 mmol/100g. This implies the soils at these areas are unstable and land-slides can occur in these areas. High exchange acidity and high concentration of Na^+ ions will destroy soil colloids and expose the charges.

There was a significant positive correlation (r = 0.928, $P < 0.01$) between Ca and Mg. This could be attributed to the fact that they owe their origin

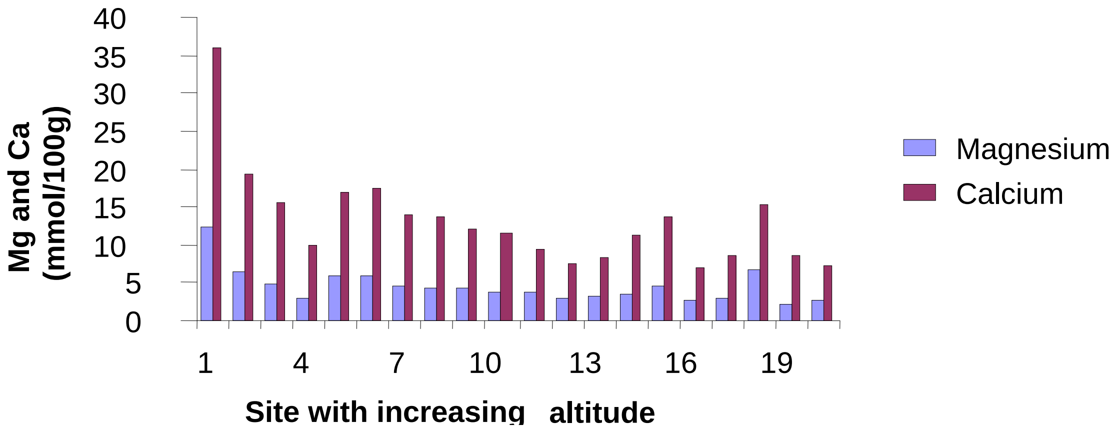

Figure 5. Magnesium and calcium concentrations in soils with altitude.

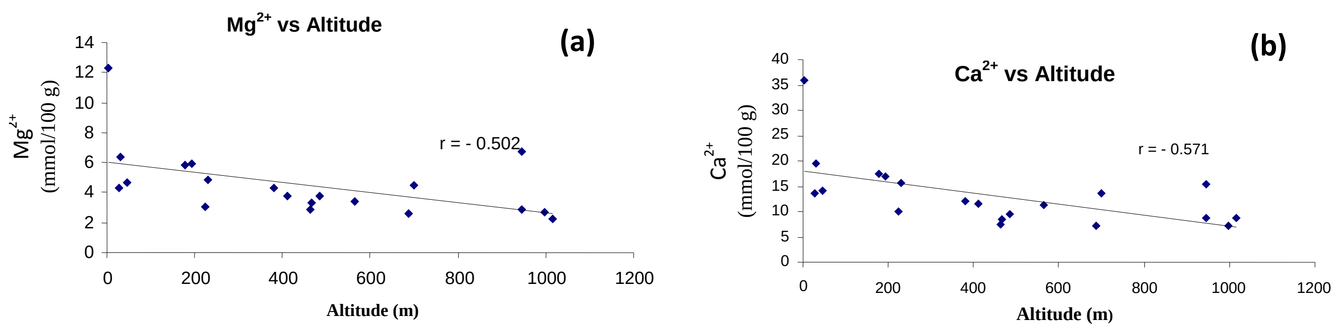

Figure 6. Relationships between calcium (a) and magnesium (b) and altitude.

from the same source probably the basaltic rocks of this area. This was same with potassium and sodium. Another significant positive correlation exists between ECEC and Mg (r=0.983, P<0.01) and between ECEC and Ca (r=0.997, P<0.01).

There was also a relation between calcium and available phosphorus though not significant. This implies they could probably have same origin.

With the exception of two samples, 17 and 18 (values 6.30 and 4.74%, respectively) in Bokwango that had adequate organic carbon, the rest had organic carbon less than 4%, which is low. This confirms the results of Nkweteyim (1999) where organic carbon ranged from 0.54 to 6.22%). Generally, with the exception of Bokwango and Vasingi the lower regions had high cultivation and housing activities going on, so much of the organic carbon in these places had been used up. Except in Mile 14 where carbon in both cultivated and non-cultivated areas was the same, 3.12% in all other towns the carbon in the non-cultivated area was higher than in the cultivated area. There was a significant positive correlation (r = 0.71, p <0.01) between organic carbon and altitude. This could be allied to the fact that as one moves higher the mountain vegetation abundance increases as much has been cut down at lower elevations for construction. Carbon is an essential component of plant bodies.

Most of the soils had total nitrogen less than 0.5%. This supports previous results of Nkweteyim (1999) in which total nitrogen ranged from 0.05 to 0.52% in the same region. The highest was at Bokwango, sample 17, uncultivated. This could be attributed to the non–cultivation of the area and less human activities. There was a significant positive relationship (r = +0.54, p < 0.05) between altitude and total nitrogen a probable reflection of an increase in vegetation intensity as the Mountain is ascended as in Carbon. This is confirmed by the positive correlation between total nitrogen and organic carbon with a positive correlation coefficient (r = +0.74, p < 0.01).

Based on the critical range of available P (10-15 mg P kg^{-1}) set by Tchuenteu (1994) for volcanic soils, available P was generally higher than this value in the soil obtained at Down Beach which could be attributed to the fact that no farming takes place in this area to deplete the

Table 4. Physicochemical properties of soils from cultivated portions of the study area.

S/N	Moist content	pH		Org. C	Tot. N	C/N	Avail. P	Exchangeable bases				Exch. acidity	ECEC	BS	Sand	Silt	Clay	Textural class*
								Ca	Mg	K	Na							
	(%)	H_2O	KCl	(%)		(mg/kg)		mmol/100g							(%)			
2	16.82	5.93	4.77	1.54	0.11	14	1	19.41	6.40	0.33	0.04	0.34	26.52	98.72	33.0	29.8	37.2	C L
3	16.41	6.03	4.90	2.27	0.12	19	2	15.61	4.87	0.65	0.08	0.31	21.52	98.56	34.6	31.0	34.4	CL
5	9.64	6.23	5.21	1.98	0.26	8	45	17.00	5.89	0.82	0.11	0.25	24.07	98.96	47.7	35.7	16.6	L
7	12.26	6.26	4.99	1.87	0.12	16	23	14.09	4.69	0.37	0.08	0.20	19.43	98.97	35.5	40.6	23.9	L
10	17.60	6.24	5.18	3.12	0.28	11	5	11.51	3.74	0.82	0.06	0.11	16.24	99.32	32.2	30.6	37.2	CL
12	14.44	5.85	4.46	1.99	0.09	22	38	7.51	2.85	0.22	0.07	0.31	10.96	97.17	21.7	48.7	29.6	CL
13	21.99	5.60	4.46	2.45	0.48	5	29	8.35	3.32	0.68	0.13	0.87	13.35	93.48	32.4	43.7	23.9	L
16	12.42	6.09	4.78	3.22	0.24	6	12	7.09	2.59	0.37	0.05	0.44	10.54	95.83	31.1	49.8	19.1	L
18	21.19	5.80	4.40	4.74	0.58	8	11	15.38	6.69	0.28	0.04	0.52	22.91	97.73	28.6	46.3	25.1	L
19	20.60	6.18	5.00	3.03	0.12	25	4	8.66	2.22	1.69	0.18	0.25	13.00	98.10	31.7	41.6	26.6	L
Av	16.34	6.02	4.82	2.62	0.24	13.4	17	12.46	4.33	0.62	0.08	0.36	17.85	97.68	32.85	39.78	27.36	

*L=loam, CL=clay loam, C=clay.

Table 5. Physicochemical properties of soils non-cultivated portions of the study area.

S/N	Moist content	pH		Org. C	Tot. N	C/N	Avail. P	Exchangeable bases				Exch. acidity	ECEC	BS	Sand	Silt	Clay	Textural class*
								Ca	Mg	K	Na							
	(%)	H_2O	KCl	(%)		(mg/kg)		mmol/100g							(%)			
1	14.87	6.15	5.09	1.92	0.21	9.00	65.00	35.84	12.28	0.64	0.07	0.29	49.12	99.41	36.40	40.60	23.00	L
4	17.32	5.83	4.80	2.78	0.18	15.00	11.00	10.04	3.02	0.39	0.06	0.43	13.94	96.92	46.00	31.10	22.90	L
6	13.59	6.22	5.04	2.45	0.26	9.00	51.00	17.52	5.84	1.59	0.15	0.26	25.36	98.98	46.20	35.40	18.40	L
8	14.50	5.84	4.42	1.67	0.11	15.00	4.00	13.68	4.31	0.90	0.07	0.42	19.38	97.83	29.70	42.20	28.10	CL
9	17.83	6.02	4.93	3.12	0.28	11.00	3.00	12.02	4.34	0.33	0.05	0.29	17.03	98.30	37.00	32.60	30.40	CL
11	19.90	6.05	4.71	2.00	0.16	13.00	1.00	9.43	3.77	0.95	0.07	0.49	14.71	96.67	13.40	32.10	54.50	C
14	19.01	6.01	4.47	2.07	0.54	4.00	34.00	11.28	3.42	1.27	0.12	0.51	16.60	96.93	38.10	41.00	20.90	L
15	13.42	6.71	5.30	3.72	0.54	7.00	35.00	13.65	4.53	1.99	0.19	0.33	20.69	94.41	38.70	46.30	15.00	L
17	20.48	6.18	5.08	6.30	0.71	9.00	53.00	8.65	2.87	1.07	0.12	0.57	13.28	95.71	28.50	42.00	29.50	CL
20	18.17	5.77	4.60	2.88	0.25	12.00	10.00	7.16	2.72	0.99	0.09	0.58	11.54	94.97	32.403	46.80	20.80	L
Av	16.91	6.08	4.84	2.89	0.32	10.40	26.70	13.93	4.71	1.01	0.10	0.42	20.17	97.01	4.60	39.00	26.40	

*L=Loam, CL=clay loam, C=clay.

Table 6. Correlation coefficients between physicochemical properties of soils examined.

Indices	Moist	pH (H_2O)	Org. C	Tot. N	Av. P	Ca	Mg	K	Na	Ex.ac	ECEC	BS	Clay	Silt	Sand
Moist-pH (H_2O)	-0.47*	-													
Org. C	0.40	0.17	-												
Tot. N	0.39	0.13	0.75**	-											
Av. P	-0.30	0.31	0.14	0.39	-										
Ca	-0.31	-0.23	-0.29	-0.13	0.43	-									
Mg	-0.26	0.15	-0.23	-0.06	0.42	0.93**	-								
K	0.038	0.57**	0.17	0.29	-0.25	-0.06	-0.15	-							
Na	0.02	0.49*	0.17	0.33	0.40	-0.13	-0.21	0.89**	-						
Ex. ac	0.57**	0.61**	0.25	0.50*	0.02	-0.35	-0.26	-0.05	0.06	-					
ECEC	-0.29	0.24	-0.26	-0.09	0.45*	0.99**	0.98**	-0.02	-0.09	-0.32	-				
BS	-0.34	0.19	-0.35	-0.50*	-0.03	0.57**	0.51*	-0.23	-0.34	-0.79**	0.53*	-			
Clay	0.42	-0.19	-0.12	0.30	0.50*	-0.11	-0.09	-0.24	-0.42	-0.04	-0.12	0.19	-		
Silt	-0.05	-0.07	0.29	0.33	0.30	-0.24	-0.17	0.10	0.24	0.38	-0.21	0.55*	0.52*	-	
Sand	-0.44	0.27	0.10	0.07	0.33	0.32	0.24	0.19	0.28	-0.27	0.31	0.24	0.71**	0.24	-
Alt	0.53*		0.71**	0.54*		-0.57*	-0.50*				0.53*				

*, **Significant at 5 and 1% levels, respectively.

phosphorus. In some areas the high values of available P could partly be due to the residual levels from previous P fertilization. According to Wild (1996), the absorbed nature of phosphates by soils makes the concentration in drainage water low even where phosphate fertilizers are applied.

The ECEC and altitude showed a negative correlation (r= -0.53, P > 0.05). This could be attributed to weathering. At higher altitudes there is weathering and the ions move downwards. Nitrogen and altitude showed a positive correlation (r=0.54, P < 0.05). This was same for organic carbon and altitude (r=0.708 P<0.01). This was confirmed in the significant correlation between organic carbon and nitrogen (r=0.74, P < 0.01). The soils generally had high CEC. CEC can directly influence the changes in soil pH, because every time the clay particles capture cations, they release H^+ and Al^{3+} ions, which in high concentrations acidifies soil. Generally, tropical soils have low CEC, especially for high sandy and low pH soils. Tropical soils have a high humidity and acidity, contributing to an overall increase of CEC (Aprile et al., 2012).

The increase in carbon and nitrogen with height could be attributed to anthropogenic actions such as construction of houses and farming which are more common at the lower altitudes where there was more habitation. The higher carbon at higher altitude could also be attributed to above ground litter fall and root mortality which are the two primary processes that contribute to soil carbon inputs along an elevation gradient (Yang et al., 2009; Charan et al., 2012). In a similar study, Ji et al. (2015) found that soil organic carbon contents and stocks were significantly higher at the high-altitude site than a low altitude site in the entire soil profile (0-60 cm). In another similar study, Charan et al. (2013) suggested altitudinal variations in soil physico-chemical properties at cold desert high altitude.

Physicochemical properties of water from study area

The results of water analysis are shown in Table 7 and the correlations are shown in Table 10. The pH of the water samples ranged from 6.16 to 8.54. The streams had generally higher pH than wells. This is could be due to the deposition of alkaline wastes into water sources or runoffs. The low pH in the wells could partly be attributed to the fact

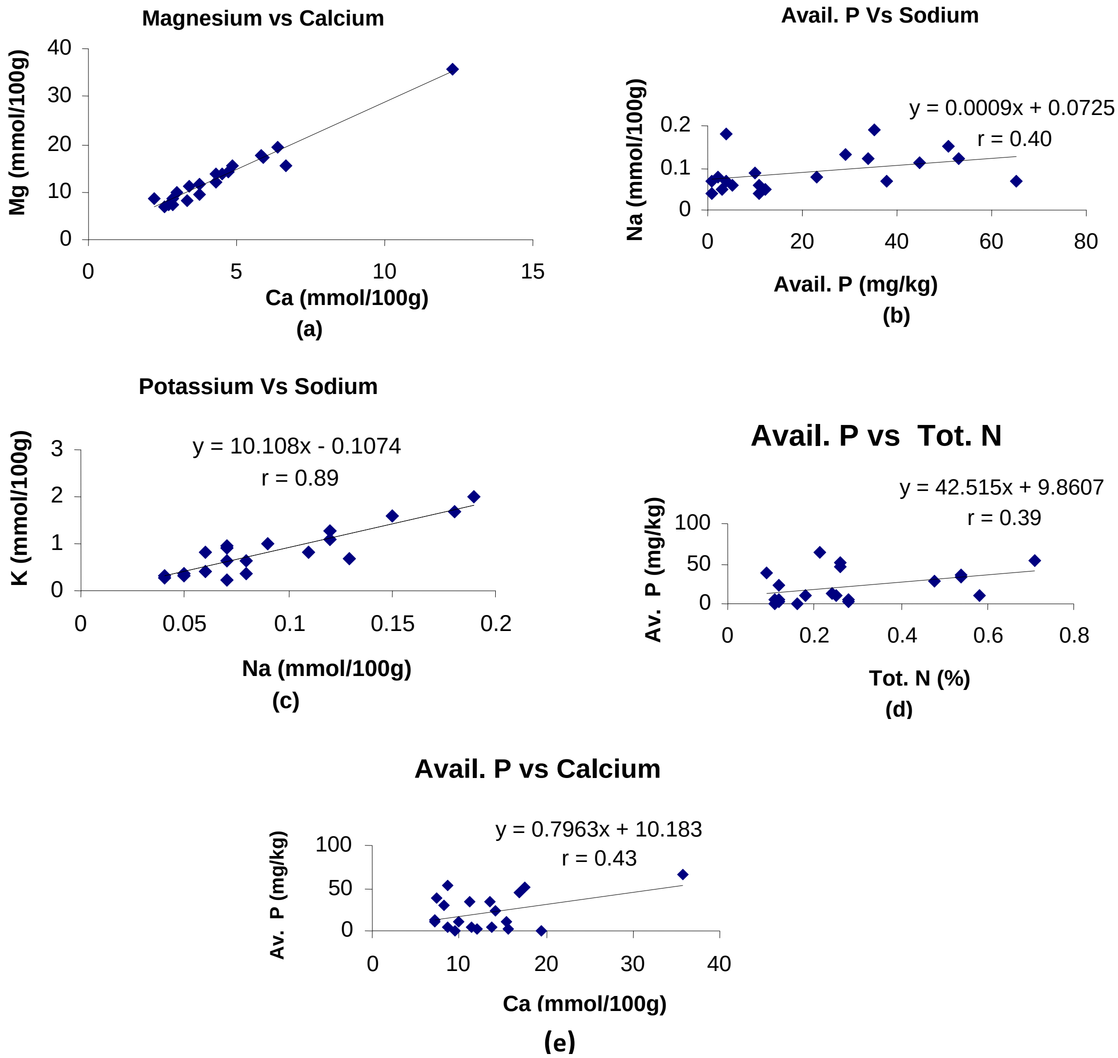

Figure 7. Relationships between some soil properties.

that tropical soils have colloids which are positively charged (Rowel, 1994). The average pH in the region was 7.7 which is within the range recommended by EU, Canada and USA, 6.5-8.5 (Chapman, 1997).

Nitrates were generally absent in most of the samples but the concentrations ranged between 0 to 4.93 mg/L. The average nitrate concentration in streams was 0.31 mg/L, 1.94 mg/L in wells and 0.68 mg/L in springs.

Samples 5 to 10 that is, between Tiko and Wonya-Mavio, Buea had nitrate. This implies water from these areas is unsafe for drinking. The highest concentration of 4.93 mg/L was obtained from a well at Wonya-Mavio. This may be attributed to farming, soil type and distance from two neighbouring toilets. Nitrate is detrimental to the health of humans especially children as it leads to methamoglobinaemia. Nitrates concentration increased with an increase in altitude, an indication of addition of this property from the mountain probably released from this active volcano. The sulphate concentration was generally low in the region. However the highest, 5.28 mg/L was recorded at well at Douala road, Tiko. This could be attributed to effluents from the rubber factory.

Bicarbonate and magnesium showed a positive significant relation ($P < 0.01$; Figure 8d). This could be because both have the same origin which is natural. Temperature and sulphate showed similar correlation ($P < 0.01$, Figure 8e). This could be attributed to the non-dissolution of sulphates at higher temperatures. There was little or no carbon and nitrogen cycling and transfer from the high-altitude soils to the low-altitude waters since the low-altitudes waters had low values of nitrate and bicarbonate (Table 7). This implies the carbon in the

Table 7. Physicochemical properties of water sources from West Flank of Mount Cameroon.

S/N	Na^+	K^+	Mg^{2+}	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	HPO_4^{2-}	Elect. Cond.	pH	TDS	Temp
	mg/L								(µs/cm)		(ppm)	(°C)
1	0.23	0.78	13.44	168.36	0.00	2.55	4.00	0.00	336	7.24	168	28.3
2	0.23	2.26	11.64	145.18	0.00	3.68	25.00	0.03	302	7.59	150	30.7
3	015	3.74	12.84	189.10	0.00	3.73	23.00	0.36	320	7.38	160	31.7
4	0.07	1.09	12.36	153.72	0.00	2.61	1.00	0.10	362	7.44	133	27.5
5	0.15	0.04	7.68	69.54	0.90	5.28	4.50	0.04	210	7.12	102	28.9
6	0.15	1.09	10.20	97.60	0.80	4.03	2.00	0.20	225	8.34	112	29.6
7	0.60	1.87	13.8	118.34	1.01	3.38	0.00	0.12	232	8.30	116	28.9
8	0.07	0.78	8.64	79.30	0.65	1.84	0.00	0.06	347	8.54	188	25.9
9	0.07	0.39	3.96	39.04	0.65	1.31	2.00	0.00	297	8.04	140	24.9
10	0.07	1.09	5.04	24.40	4.93	3.44	2.00	0.01	129	7.71	64	25.1
11	0.15	0.39	2.88	34.16	0.00	1.42	0.00	0.02	236	7.75	118	24.3
12	0.15	1.48	10.44	9.39	0.00	2.25	0.00	0.00	257	8.31	130	25.8
13	0.15	1.09	11.28	124.44	0.00	2.73	0.00	0.04	315	7.22	151	28.5
14	0.07	0.39	5.28	58.56	0.00	1.93	0.00	0.15	285	7.76	187	27.5
15	0.07	0.00	9.12	54.90	1.17	2.08	2.00	0.02	228	6.80	150	23.3
16	0.37	2.65	12.72	170.80	000	1.78	14.00	0.04	315	7.55	235	25.5

form of carbonates or bicarbonates and nitrogen in the form of nitrates were trapped by the positive charges on the soil colloids.

The results of ground water and surface water presented in Tables 8 and 9 respectively. Apart from Nitrate whose mean concentration decreased from 1.0 mg/L in ground water to 0.31 mg/L in surface water; all the other properties had mean values significantly higher in surface water than in ground water (Tables 8 and 9). A lot of farming is being done around surface water and there indiscriminate dumping of various types of waste in streams. This difference in properties could be attributed to anthropogenic sources of pollution. They include among others; fertilizers, herbicides and insecticides, office wastes, wastes from construction sites, car washing points, garages, petroleum filling stations and household wastes.

Sources of water and soil pollution in the study area

From the results of the water analysis, Na^+, K^+ and Mg^{2+} were comparatively higher at Beach Limbe than the other sources. This could be attributed to natural sea water intrusions and or weathering and movement of these substances from high altitude to low altitude. Correlation analysis indicated that magnesium had a significant negative correlation ($P > 0.05$) with altitude, an indication that this entity and its associates have as a major source natural weathering and transportation from uphill. River Benyo had a high magnesium concentration more than other parameters. Sources of magnesium in this stream could be from the weathering of rocks present in this stream.

According to Endeley et al. (2001), the area is composed mainly of massive basaltic lava flows and the geochemistry of volcanic rocks from the entire Cameroon Volcanic Line (CVL) shows that the rocks have MgO > 4%. The weathering of the volcanic rocks might therefore be expected to lead to the presence of elevated level of this species in the stream. Another probable contributor of magnesium in this stream is anthropogenic due to the deposition of waste such as metallic objects, plastics etc. and laundry activities that go along the stream. Nitrates had the highest value (4.93 mg/L) at the Wonya Mavio well. This could be

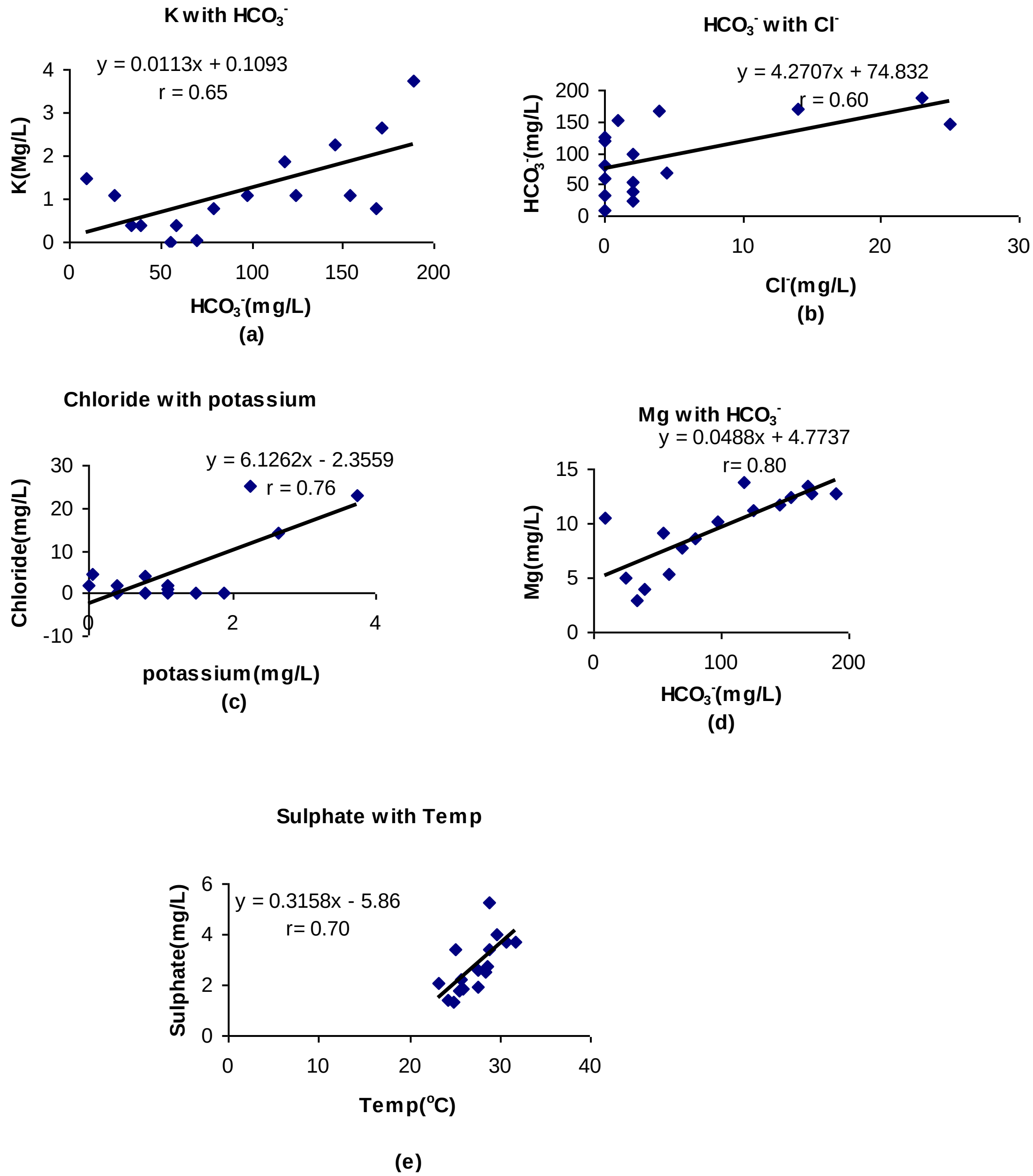

Figure 8. Relationships between some physicochemical properties of water.

allied to anthropogenic sources such as the use of nitrogenous fertilizers and/or intrusion of domestic sewage. Apart from residencies, there is a small garden at this point of sampling with probable usage of nitrogenous fertilizers. Wernick et al. (1998) found out a positive relationship between residential and agricultural activities on elevated nitrates in the Salmon River of British-Colombia. High nitrates are undesirable in water bodies as they can result in eutrophication and methemoglobinemia (Kross, 1993).

The highest sulphate value of 5.28 mg/L was obtained from the well in Tiko. This could be attributed to anthropogenic sources probably due to the fact that this well is located near the rubber factory. Rubber effluents have high content of organic matter which is one of the major sources of sulphates. According to Rose et al. (1979), the concentration of sulphate in rainwater ranges between 1 to 3 mg/L. Therefore, the concentration of sulphate in this well which is higher than the range in rainwater confirms the fact that sulphates are probably being added into this system by anthropogenic activities. Chlorides concentrations were higher in Limbe waters

Table 8. Physicochemical properties of ground water sources from West Flank of Mount Cameroon.

S/N	Na^+	K^+	Mg^{2+}	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	HPO_4^{2-}	Elect. Cond.	pH	TDS	Temp
	mg/L								(µs/cm)		(ppm)	(°C)
1	0.23	0.78	13.44	168.36	0.00	2.55	4.00	0.00	336.00	7.24	168	28.3
4	0.07	1.09	12.36	153.72	0.00	2.61	1.00	0.10	362.00	7.44	133	27.5
5	0.15	0.04	7.68	069.54	0.90	5.28	4.50	0.04	210.00	7.12	102	28.9
9	0.07	0.39	3.96	039.04	0.65	1.31	2.00	0.00	297.00	8.04	140	24.9
10	0.07	1.09	5.04	024.40	4.93	3.44	2.00	0.01	129.00	7.71	64	25.1
11	0.15	0.39	2.88	034.16	0.00	1.42	0.00	0.02	236.00	7.75	118	24.3
15	0.07	0.00	9.12	054.90	1.17	2.08	2.00	0.02	228.00	6.80	150	23.3
16	0.37	2.65	12.72	170.80	0.00	1.78	14.00	0.04	315.00	7.55	235	25.5
H	0.37	2.65	13.44	170.80	4.93	5.28	14.00	0.10	362.00	8.04	235	28.9
L	0.07	0.00	2.88	024.40	0.00	1.31	0.00	0.00	129.00	6.80	64	23.3
Av	0.15	0.80	.40	089.37	1.00	2.56	3.69	0.03	264.13	7.46	139	26.0

H=Highest value; L=Lowest value; Av=mean.

Table 9. Physicochemical properties of surface water sources from West Flank of Mount Cameroon.

S/N	Na^+	K^+	Mg^{2+}	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	HPO_4^{2-}	Elect. Cond.	pH	TDS	Temp
	mg/L								(µs/cm)		(ppm)	(°C)
2	0.23	2.26	11.64	145.18	0.00	3.68	25.00	0.03	302	7.59	150	30.7
3	015	3.74	12.84	189.10	0.00	3.73	23.00	0.36	320	7.38	160	31.7
6	0.15	1.09	10.20	097.60	0.80	4.03	2.00	0.20	225	8.34	112	29.6
7	0.60	1.87	13.80	118.34	1.01	3.38	0.00	0.12	232	8.30	116	28.9
8	0.07	0.78	08.64	079.30	0.65	1.84	0.00	0.06	347	8.54	188	25.9
12	0.15	1.48	10.44	009.39	0.00	2.25	0.00	0.00	257	8.31	130	25.8
13	0.15	1.09	11.28	124.44	0.00	2.73	0.00	0.04	315	7.22	151	28.5
14	0.07	0.39	05.28	058.56	0.00	1.93	0.00	0.15	285	7.76	187	27.5
H	0.60	3.74	13.80	189.10	1.01	4.03	25.00	0.36	347	8.54	188	31.7
L	0.072	0.391	05.28	009.39	0.00	1.84	0.00	0.00	225	7.22	150	25.8
Av	.05	.59	10.52	102.74	0.31	3.00	6.25	0.12	285	7.93	149	28.6

H=Highest value; L=lowest value; Av=mean.

than in other samples. This might have resulted from natural processes of sea water intrusion and sea sprays as the area is proxy to the sea. Concomitantly, higher chlorides of this area were masked by high potassium concentrations. According to Chapman (1997), potassium salts are widely used in industries. This is an indication that industries found within this municipality constitute major sources of water pollution. Similar

Table 10. Correlation coefficients between physicochemical properties of water samples examined.

	Alt	Na	K	Mg	HCO_3^-	NO_3^-	SO_4^{2-}	Cl^-	HPO_4^-	EC	pH	TDS	T
Alt	-												
Na	-0.22	-											
K	-0.32	0.45	-										
Mg	-0.49	0.56*	0.61*	-									
HCO_3^-	-0.69**	0.41	0.65**	0.80**	-								
NO_3^-	0.28	-0.14	-0.17	-0.35	-0.42	-							
SO_4^{2-}	-0.55*	0.17	0.21	0.30	0.24	0.25	-						
Cl	-0.40	0.18	0.76**	0.39	0.60*	-0.21	0.32	-					
HPO_4^{2-}	-0.24	0.06	0.56*	0.30	0.45	-0.18	0.35	0.37	-				
EC	-0.37	-0.03	0.27	0.45	0.62*	-0.75**	-0.36	0.25	0.16	-			
pH	0.11	0.18	0.09	-0.13	-0.31	0.05	-0.18	-026	0.08	-0.04	-		
TDS	-0.11	0.12	0.28	0.32	0.48	-0.62*	-0.49	0.30	0.09	0.73**	-0.07	-	
Temp	-0.78**	0.29	0.55*	0.56*	0.64**	-0.29	0.70**	0.55*	0.64**	0.25	-0.03	-0.01	-

*, **Significant at 5 and 1% levels, respectively.

high values were obtained by Mafany (2000) in the Douala Municipality sampling fresh water bodies.

The pollutants likely originate from natural sources (volcanic rocks that weather) and sea intrusions but also from anthropogenic sources (waste, use of chemicals in CDC industry, laundry activities etc).

The new soil and water data shall help improve the livelihood of the people living along the area. They show that nitrogen and carbon increase with altitude and consequently cultivation shall yield more crops at higher altitudes. They also indicate that the highest nitrate was found in Wonya-Mavio, a village in Buea. The people living here would restrict the use of nitrogenous fertilizers and be careful of intrusion of domestic sewage.

Conclusion

All the soils in the region were acidic. Most of the physicochemical properties of the water analysed were within acceptable limits of WHO. Nitrates were generally absent in most of the samples. The water sources between Tiko and Wonya-Mavio, Buea had higher nitrate. There were significant positive relationships ($p < 0.05$ and $p < 0.01$) between nitrogen and altitude and carbon and altitude, respectively. Magnesium and ECEC showed a significant negative correlation ($p < 0.05$) with altitude while calcium showed a highly significant negative correlation with altitude. Among the natural sources of pollution identified are weathering, erosion and sea water intrusions. The anthropogenic ones include wastes from homes, laundry, fertilizers, sewage and factories.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Activity concentrations and dose assessment of ^{226}Ra, ^{228}Ra, ^{232}Th, ^{40}K , ^{222}Rn and ^{220}Rn in soil samples from Newmont-Akyem gold mine using gamma-ray spectrometry

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In this study 14 soil samples were measured for natural radioactivity levels including radon-222 (^{222}Rn) and radon-220 (^{220}Rn) concentration at Akyem-Gold Mine premises, surrounding communities in Ghana. Both radon and radioactivity concentrations of radium-226 (^{226}Ra), thorium-232 (^{232}Th) and potassium-40 (^{40}K) were determined by means of gamma spectrometry system equipped with high purity germanium detector. The studied samples gave natural radioactivity levels of 28, 12 and 11 Bq/kg, respectively compared to global ^{226}Ra, ^{232}Th, and ^{40}K concentrations of 37, 33 and 400 Bq/kg, respectively, according to UNSCEAR (2000) report. The annual effective dose rate (AED) due to external and internal gamma exposure ranged from 0.060 to 0.18 mSvy^{-1} with a mean value of 0.11 ± 0.03 mSvy^{-1} compared to the recommended value of 1 mSvy^{-1}. There is a correlation between ^{226}Ra and ^{222}Rn in soil gas with a good linear coefficient of (R^2 =1). The availability of ^{226}Ra and ^{222}Rn shows that there is a source of uranium-238 (^{238}U) and thorium-232 (^{232}Th) bearing minerals within the adjacent geologic units of Akyem. This implies that most of the radon in the soil gas comes from ^{226}Ra. The assessment of radium equivalent activity varied from 19.71 to 69.88 Bq/kg with mean value of 37.53 ± 15.51 Bq/kg lower than the global limit of 370 Bq/kg. The internal hazard index ranged from 0.07 to 0.25 Bq/Kg with a mean value of 0.13 ± 0.05 Bq/Kg, also lower than the accepted value of unity, while external hazard index ranged from 0.05 to 0.19 Bq/Kg with a mean value of 0.10 ± 0.04 Bq/Kg.

Key words: Radon, thoron, natural radioactivity**,** annual effective dose, radium equivalent index, external and internal hazard index.

INTRODUCTION

Humans are exposed to ionizing radiation from natural sources which are on a large scale in the earth's environment and remains in several geological formations in soils, rocks, plants, water and air. The public exposures to ionizing radiation include natural radiation sources such as cosmic and terrestrial radiation.The exposure pathways include external irradiation, inhalation or ingestion. Information on radioactivity levels in soil is necessary for the estimation of possible radiological hazards to human health**.** Studies have shown that over 50% of total radiation exposure comes from radon (USEPA, 2007).

There are several isotopes of radon but ^{222}Rn (Radon) and ^{220}Rn (Thoron) are of interest because of their availability in the environment due to their negative health impacts on the humans. Each nuclide has its own contribution to radiation exposure, for instance radon's half-life of 3.8 days is adequate enough to diffuse into the indoor environment and bring a rise in indoor concentration. On the contrary the half-life of thoron is only 56 seconds which implies that its presence is limited to close proximity (Yamada et al., 2006). However, recent studies in some countries have shown that in certain circumstances the doses from thoron and its progeny are notable and comparable to those from radon (Sciocchetti et al., 1992).

Uranium (^{238}U) and Thorium (^{232}Th) are the ultimate progenitors of ^{222}Rn (Radon), ^{220}Rn (Thoron), respectively. The immediate mother radionuclides of radon, thoron are radium-226, radium-224, respectively. Despite the fact that Rn-220 comes from the disintegration of Ra-224, it is often characterized as a decay product of Ra-228, which is a longer- lived parent ($t_{1/2}$ = 5.75y), commonly analyzed in the environmental samples such as soil and water.

Exposures to natural sources are often not much for safeguard concern. However, there are conditions where exposures to natural sources of radiation may need attention if some measures are not followed. A good scenario is the accumulation of high concentrations of radon and thoron in air. Another case is the mining and/or processing of mineral ores or materials where the activity concentrations of radionuclides of natural origin in the material itself, or in any substance arising from the process, are significantly elevated. Such materials have come to be called Naturally Occurring Radioactive Materials (NORM) (IAEA, 2005).

The radionuclides embedded in bedrocks are weathered off chemically or physically and by means of transportation they end up deposited in rivers, lakes or seas. Other human practices such as mining and mineral processing increase the concentration of both end products or wastes to produce Technologically Enhanced Naturally Occurring Radioactive Material (TENORM). Both NORM/TENORM contain materials with a lot of radioactive elements found in the environment, such as ^{238}U, ^{232}Th series and their progenies ^{228}Ra, ^{224}Ra, ^{226}Ra as well as ^{40}K. These radioisotopes can pollute the environment and bring constraints to public well-being (Peroni et al., 2012).

While mining has been seen as one of the principal sources of exposure to NORM/TENORM, the mining companies are not given guidelines for these radioactive materials in most countries due to insufficient safeguards for their regulation by the Regulatory Authorities. The health concern of NORM/TENORM is focused primarily on the production and release of radon, thoron gases produced through the radioactive decay of ^{226}Ra, ^{224}Ra, respectively. The inhalation of radon has been accompanied with high risk of cancer of the lung (BEIR IV, 1988).

Ghana is conducting numerous mining activities which means that possibility of producing NORM which is the main source of radon and thoron gases is very enormous.

For radiation protection purposes it is preferably important to monitor the presence and concentration of radon decay products, while for the identification of the sources and origin of radon the measurement of its concentrations in air or water, and sometimes its exhalation from soil and building materials, is more significant (Tykva and Sabol, 1995).

It is critical to evaluate the soil gas radon and thoron concentrations as literature has shown that most indoor radon emanates from the soil. Therefore with mining and mineral processing activities conducted at Newmont Akyem Gold Mine, it is likely that the levels of NORMs have been elevated.

The aim of the study was to determine activity concentration and dose assessment for NORMs including soil gas radon and thoron.

Study area

The Newmont Ghana's - Akyem Gold Mine (AGM) is situated roughly three kilometers west of the district capital New Abirem,133 km west of Koforidua, the regional capital and 180 km northwest of Accra, the national capital (Akyem Gold Mining Project, 2008). Akyem in the Eastern region of Ghana is found amongst the following communities: Afosu, New Abirem, Old Abirem, Mamanso, Yayaaso, Adausena, Adjenua, Hweakwae, Ntronang and Yaw Tano. The Eastern region of Ghana covers a land area of 19,323 kilometres which constitutes 8.1% of the total land area of Ghana. It is the

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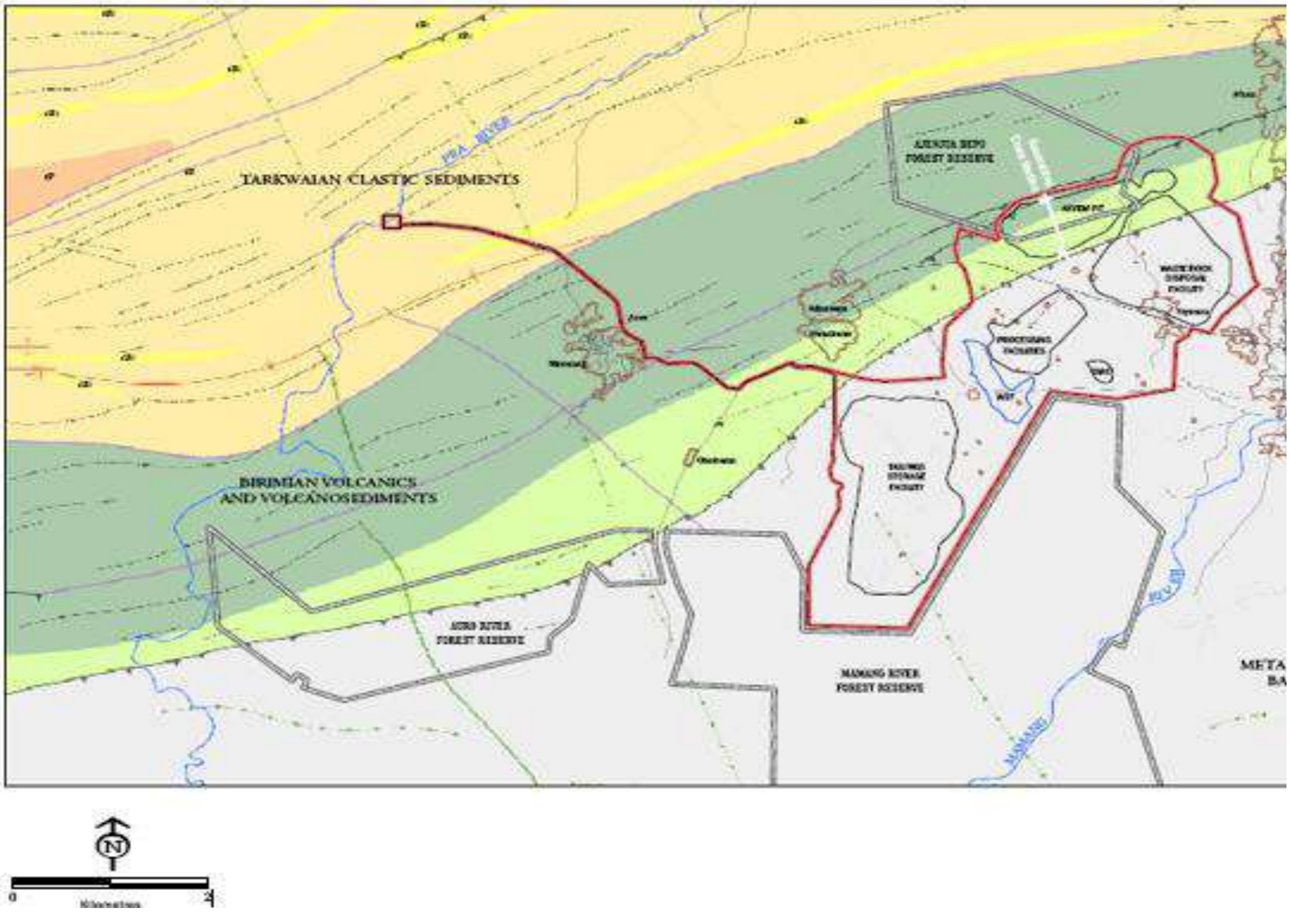

Figure 1. Geology of Akyem Study Area (AGM-EIS, 2008).

sixth largest region in terms of land area and lies between latitudes 60 and 70 North between longitudes 10 30' West and 00 30' East. The region shares common boundaries with the Great Accra, Central, Ashanti, Brong Ahafo and Volta Regions.The region contains minerals such as gold, diamond, bauxite-tantalite, limestone, kaolin and clay. Gold and diamond are however the only minerals that are being mined commercially.

The geologic section at the Akyem deposit is outlined graphically on Figure 1 and depicts rock units, the shear or thrust fault zone, ore zone, and proposed Akyem pit outline. Main geologic units in the hanging wall of the thrust fault include greywacke, a quartz-epiclastic unit, graphitic shear breccia and graphitic rubble. Mafic metavolcanics consist of the foot wall of the shear zone.

METHODOLOGY

Sampling and sample preparation

There were 14 soil samples that were randomly collected from the mining area and in the communities surrounding the mine. Figure 2 shows Akyem-Newmont Gold Mine and sample locations. The soil samples were brought to the laboratory where they were air dried in sample trays for a period of 7 days and thoroughly dried in the oven for 12 to 24 h at 105°C. The samples were then ground and sieved through a 2 mm mesh and placed into 1-litre Marinelli beakers where they were sealed and left for 30days to attain secular equilibrium between Ra-226, Th-232 and their progenies.

Calibration of HPGe and sample measurement

Gamma Spectrometry System equipped with High Purity Germanium detector coupled with Genie 2000 was used to determine ^{226}Ra, ^{228}Ra, ^{232}Th, ^{40}K, ^{222}Rn and ^{220}Rn, respectively. The aim of energy calibration was to derive a relationship between peak positions in the spectrum which correspond to gamma-ray energy. This was carried out before measuring the samples.

The energy calibration (channel number of the Multi- Channel Analyzer (MCA) versus the Gamma-ray energy) of the detector system was accomplished at a fixed gain, using standards containing known radionuclides. The standards were sealed in a container and emitted different γ-ray energies covering the range of interest from 60 keV to 1836 keV in order to test for system linearity. The standard radionuclides used for both Energy and Efficiency calibration were: Am-241 (60KeV), Cd-109 (88KeV), Ce-139 (166KeV), C0-57 (122KeV), Co-60 (1173, 1333KeV), Cs-137

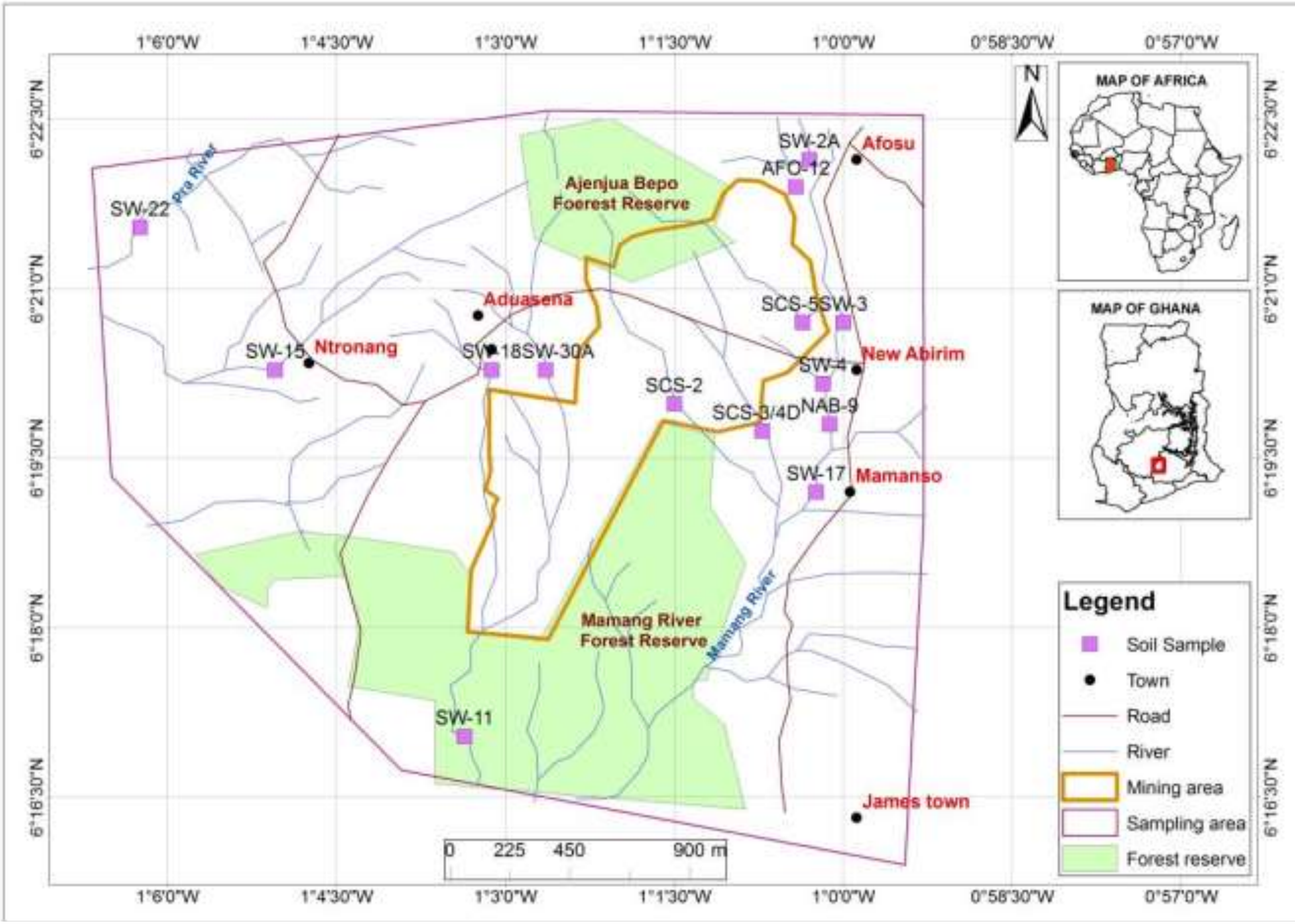

Figure 2. Layout of Akyem Gold Mine showing soil sampling points.

(662KeV), Sn-113 (392 KeV), Sr-85 (514KeV) and Y-88 (898, 1836KeV). Both Energy and Efficiency calibration were completed by firstly counting a blank Marinelli beaker with deionized water for 10 h in order to determine background radiation that was applicable in correcting the net peak area of each radionuclide analysed.

Activity concentration of ^{226}Ra, ^{228}Ra, ^{232}Th and ^{40}K

The determination of the activity concentration of each of the following radionuclides :^{226}Ra, ^{228}Ra, ^{232}Th, ^{40}K was done as follows: ^{40}K was based on the only γ-energy of 1.461Mev, ^{232}Th was taken from the sum of energies of ^{228}Ac and ^{212}Pb at energies 0.911,0.239 MeV, respectively, ^{228}Ra was according to ^{228}Ac energy, and ^{226}Ra was based on the average of ^{214}Pb , ^{214}Bi at 0.352 ,0.609 Mev, respectively. The specific activity concentrations (**C_{sp}**) of ^{226}Ra, ^{228}Ra, ^{232}Th, ^{40}K were calculated using the following equation (Darko et al, 2005; Faanu, 2011)

$$C_{sp} = \frac{N_{sam} * \exp(-\lambda Td)}{P_E \cdot T_C * \varepsilon * M_{sam}} \quad (1)$$

Where: N_{sam} is the net counts of the radionuclide in the sample, P_{E*} is the gamma ray emission probability (gamma yield), ε is the total counting efficiency of the detector system. Td is the delay time between sampling and counting, exp (λTd) is the correction factor between sampling and counting, Tc is the sample counting time and M_{sam} is mass of the sample (kg) or volume (L).

Activity concentration of radon and thoron

The specific activity concentrations Ra-226, Ra-228 were used to estimate the concentrations of Rn-222 and Rn-220 using the expression according to UNSCEAR (2000) and Nazaroff et al. (1988) in which the amount of radon, thoron [CRn-222,Rn-220], in soil gas, in the absence of radon, thoron transport is given as:

$$C_{Rn,Tn} = C_{Ra-226,228} \cdot f \cdot \rho_s \cdot \varepsilon^{-1} (1-\varepsilon)(m[K_T - 1] + 1)^{-1} \quad (2)$$

Where: $C_{Rn,Tn}$ is the radon, thoron concentration in soil (Bq/m^3), $C_{Ra-226,228}$ is the activity concentration in dry mass of ^{226}Ra, ^{228}Ra in soil (Bq/kg), F is the soil emanation factor: radon (0.2) and thoron (0.1), ρ_s is the density of soil (kgm^{-3}), ε is the porosity (0.25), m is the porosity fraction that is water filled and is zero if the soil is dry, k_T is the radon partition coefficient between water and air phases and if the soil samples are dried before measurement, then m is zero, thus the last term of equation above is omitted.

Dose and hazard assessment of natural radioactivity

Annual effective dose

Effective dose is meant for use as a safeguard quantity. The main uses of effective doses are the proposed dose assessment for planning and optimization in radiological protection, and demonstration of compliance with dose limits for regulatory objectives (ICRP, 2007). To evaluate the year-long effective dose rates, the conversion coefficient from absorbed dose in the air to effective dose ($0.7Sv.Gy^{-1}$) and outdoor occupancy factor ($0.2Sv.Gy^{-1}$) suggested by UNSCEAR (2008) was applied.

In Ghana, the average time spent indoors and outdoors (Occupancy Factors) are 0.6 and 0.4, respectively (Asumadu-Sakyi et al., 2012). According to UNSCEAR (2008), world average indoor

$$\text{Indoor effective dose rate } (mSv\ y^{-1}) = \text{Dose rate } (nGyh^{-1} \times 8760h) \times 0.4 \times 0.7\ SvGy^{-1} \times 10^{-6} \quad (3)$$

$$\text{Outdoor Effective Dose rate } (mSv\ y^{-1}) = \text{Dose rate } (nGyh^{-1} \times 8760h) \times 0.6 \times 0.7\ SvGy^{-1} \times 10^{-6} \quad (4)$$

and outdoor occupancy factors are 0.8 and 0.2, respectively. Therefore, the effective dose rate in units of $mSvy^{-1}$ was estimated using the formula according to Aguko et al. (2013); Mohanty et al. (2004) and UNSCEAR (1998).

Radium equivalent activity (Ra_{eq})

The radium equivalent activity (Ra_{eq}) is a weighted addition of activity concentration of ^{226}Ra, ^{232}Th, and ^{40}K in which the sum of their proportion is the same gamma-ray dose rates as given by the following formula (Nada, 2004):

$$Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K \quad (5)$$

Where; C_{Ra}, C_{Th} and C_K are the activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K. The coefficients 1, 1.43 and 0.077 indicate that 370 Bq/kg of ^{226}Ra, 259 Bq/kg of ^{232}Th and 4810 Bq/kg of ^{40}K produce the same gamma-ray dose rate. The above criterion only considers the external hazard due to gamma rays in building materials. The maximum recommended value of (Ra_{eq}) in raw building materials and products must be less than 370 Bq/kg for safe use. This means that the external gamma dose must be less than1.5 mSv/year.

Internal hazard index (Hin)

Another factor signifying radiological hazard due to radon is, the internal radiation exposure related to radioactivity and is expressed by the following equation (Saher et al., 2013).

$$H_{in} = C_{Ra}/185 + C_{Th}/259 + C_K/4810 \quad (6)$$

The calculation of internal hazard index was based on radon and its daughters. This is considering that, radon and its short-lived products are also hazardous to the respiratory organs. For construction materials to be considered safe for building of dwellings, the internal hazard index should be less than unity.

External hazard index (Hex)

External hazard index is also applicable when it comes to external irradiation of gamma rays from radionuclides and is given by Saher et al. (2013):

$$H_{ex} = C_{Ra}/370 + C_{Th}/259 + C_K/4810 \quad (7)$$

where C_{Ra}, C_{Th} and C_K represents activity concentration in (Bq/Kg) of ^{226}Ra, ^{232}Th and ^{40}K, respectively. In order to keep the radiation negligible, the value of Ra_{eq} must be less than 370 while H_{in} and H_{ex} must be less than unity.

RESULTS AND DISCUSSION

Concentration of soil gas radon and thoron

The results of Rn-222, Rn-220 are shown in Figures 3 and 4. The concentrations vary from 4.194 to 21.114 $kBqm^3$ with mean value of 11.362 ± 4.590 kBq/m^3 for radon and 0.544 to 13.222 kBq/m^3 with mean value of 5.062 ± 3.051 kBq/m^3 for thoron. Some research findings by Tabar et al. (2013) and others have shown that the soil gas radon concentration may differ widely due to weather pattern, conditions and soil varieties. The season of sampling may also affect radon soil concentration due to disturbance of site condition by fault movement. Table 2 compares radon results in this study with various research findings carried out around the world.

It is clear to notice that the radon values in soil gas at Akyem area are within the range of those reported in different parts of the world except a few. Moreover, the values determined in this study are much below the agreed levels according to USEPA (2005). In terms of thoron /radon ratio, Ramachandran (2010) and Giammanco et al. (2007) in studies carried out elsewhere found values of 0.530 and 0.503, respectively while this study found a mean value of 0.444 ± 0.140 which is within the range.

Correlation between radium and radon

There is correlation between Ra-226 and Rn-222 in soil gas. Figure 5(a) shows that Rn-222 is a linear function of Ra-226 with a good linear coefficient of (R^2 =1) . The availability of Ra-226 and Rn-222 shows that there is source of U-238 and Th-232 bearing minerals within the adjacent geologic units of Akyem. This implies that most

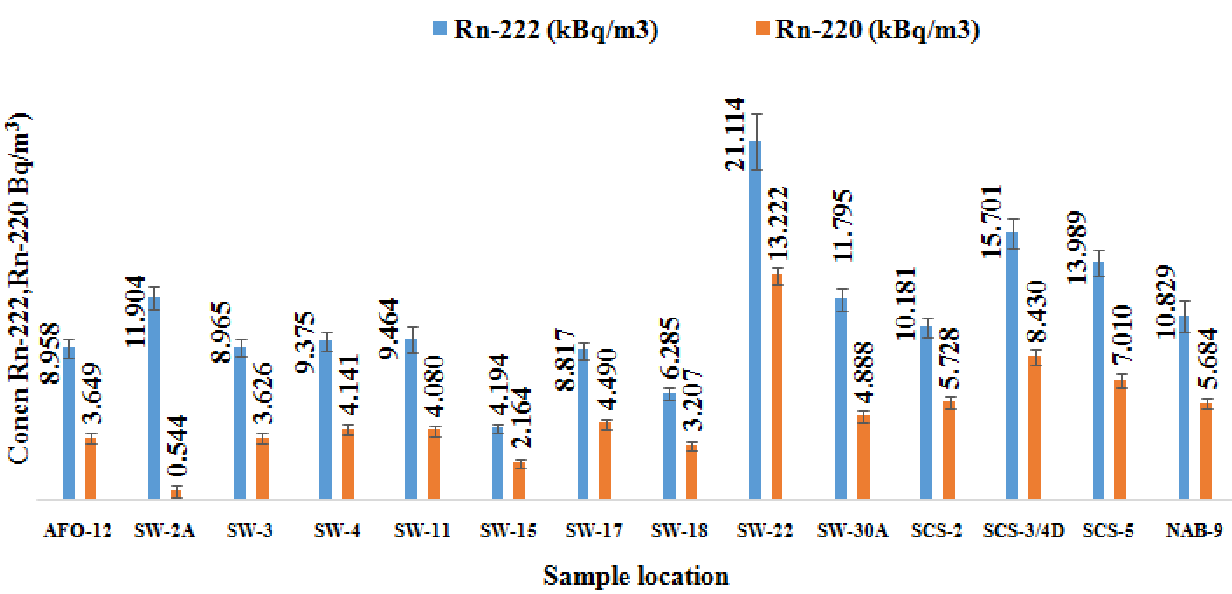

Figure 3. Rn-222 and Rn-220 concentration in soil samples.

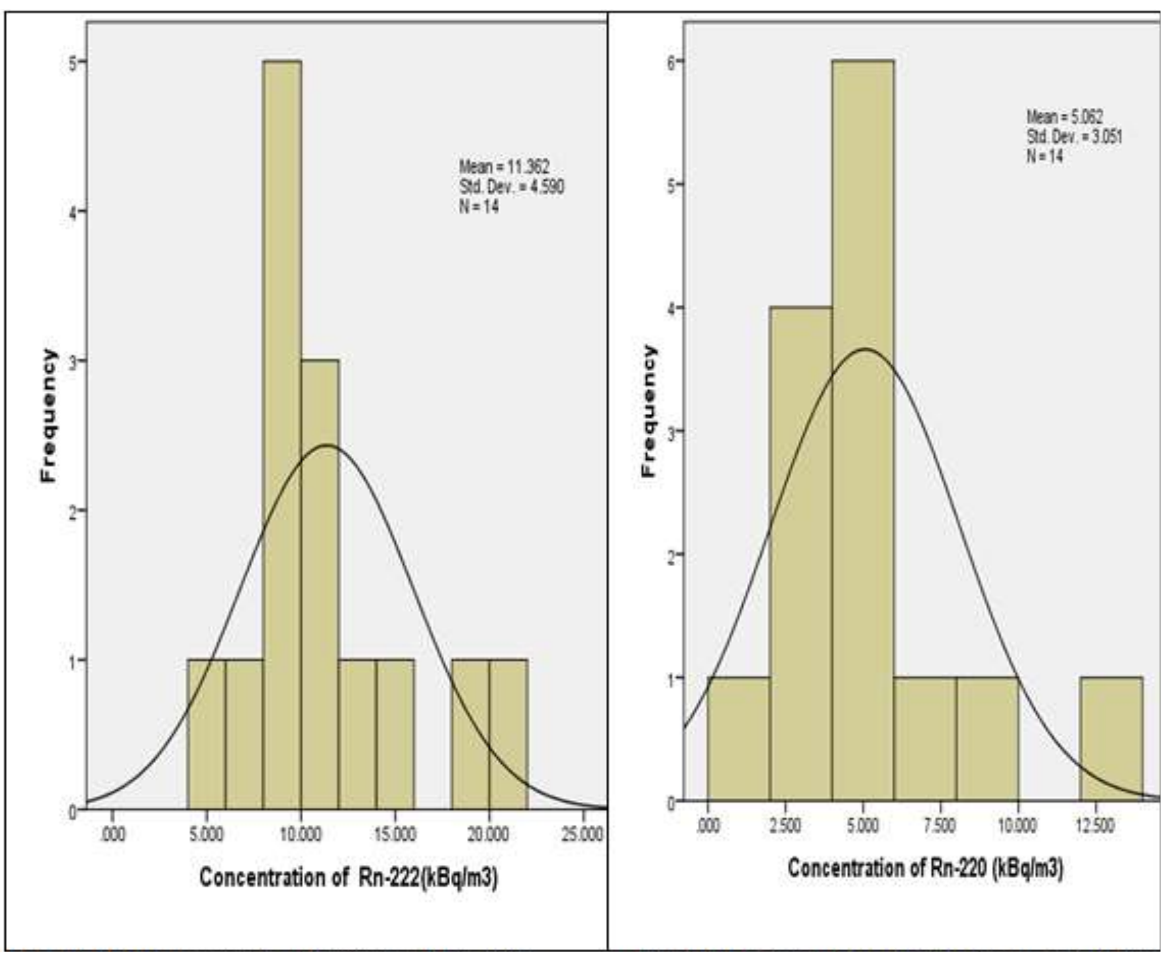

Figure 4. (a) Frequency distribution of Rn-222. (b) frequency distribution of rn-220.

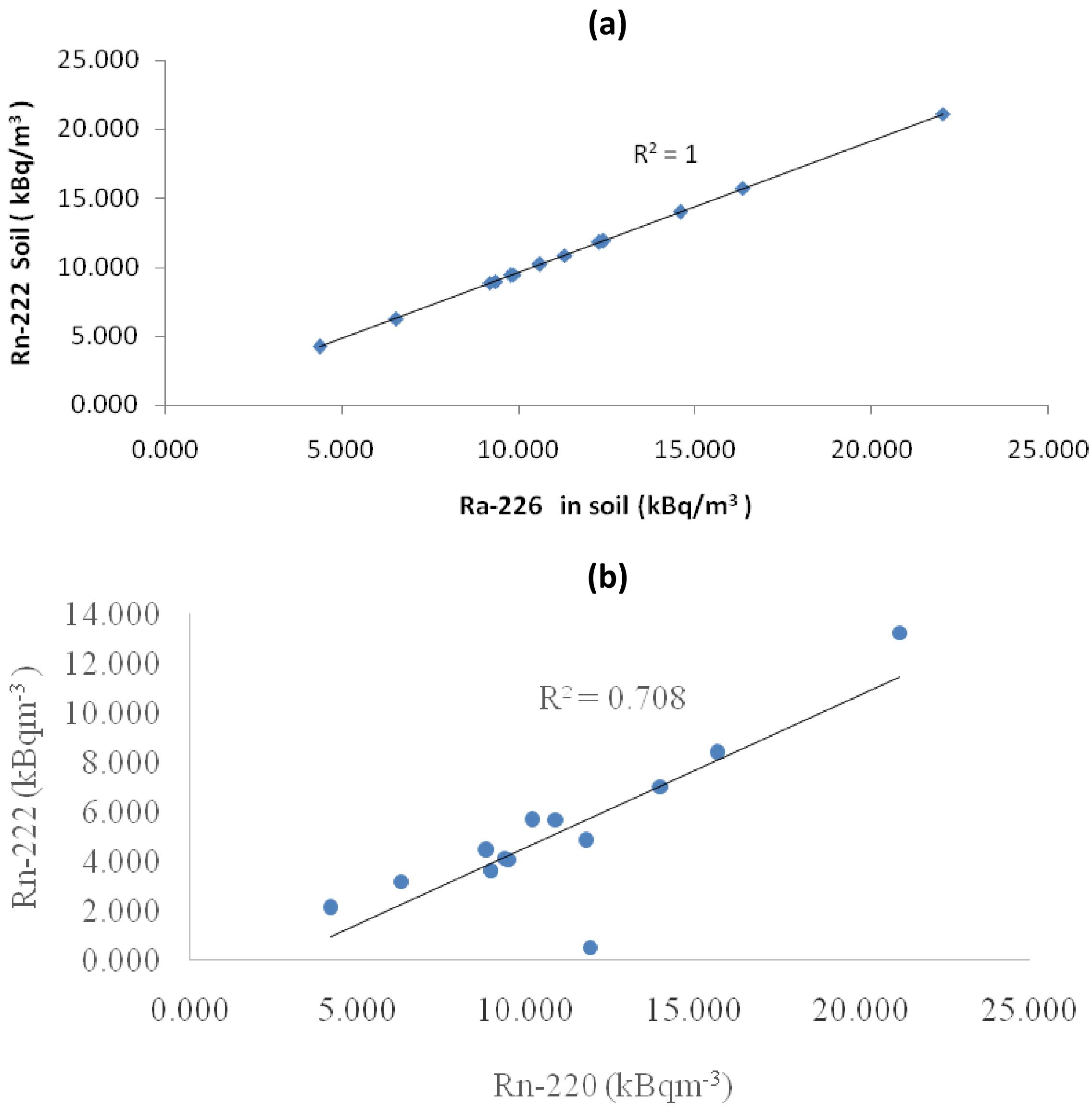

Figure 5. (a) Correlation Ra-226 and Rn-222; **(b)** Correlation Rn -222 and Rn-220.

of the radon in the soil gas comes from Ra-226. While the correlation for radon, thoron in the soil is roughly 0.7. Figure 5b shows that radon gas in the soil co-exist with thoron.

Hazard assessment due to natural radioactivity and radon in the soil

Table 1 shows that activity concentration of soil gas radon ranged from 4.194 to 21.114 kBq/m^3 with a mean value of, 10.829 ± 4.130 kBq/m^3 while for thoron, was 0.544 to 13.222 kBq/m^3 with a mean value of 5.062 ± 3.051 kBq/m^3. Soil gas radon concentration in this study compared very well with previous studies in Ghana and elsewhere (Table 2). Figure 6 depicts several averages, kurtosis and skewness coefficients and the nature of frequency statistical distribution for natural radioactivity and the measured absorbed dose rates. It is noted that the absorbed dose rates and the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K are normally distributed with mean values of 56.56 nGy/h and 11.35, 12.23, 113.78 Bq/Kg, respectively (Figure 6a to d).

Table 3 shows the average values of Radium equivalent activity (Ra_{eq}), Internal and External hazard index (H_{in}, H_{ex}) and Annual Effective Dose (mSvy^{-1}). The Ra_{eq} was calculated and ranged from 19.708 to

Table 1. Soil Rn-222 and Rn-220 concentration.

Sample Location	Concentration, Bq/Kg		Concentration, kBq/m^3	
	Ra-226	Ra-228	Rn-226	Rn-226
Afo-12	9.332 ± 0.560	7.602 ± 0.302	8.958 ± 0.538	3.649 ± 0.290
SW-24	12.400 ± 0.514	1.133 ± 0.359	11.904 ± 0.658	0.544 ± 0.345
SW-3	9.339 ± 0.402	7.554 ± 0.310	8.965 ± 0.515	3.626 ± 0.298
SW-4	9.766 ± 0.424	8.628 ± 0.310	9.375 ± 0.543	4.141 ± 0.298
SW-11	9.859 ± 0.623	8.499 ± 0.335	9.464 ± 0.798	4.080 ± 0.322
SW-15	4.369 ± 0.226	4.509 ± 0.232	4.194 ± 0.289	2.164 ± 0.223
SW-17	9.185 ± 0.400	9.354 ± 0.329	8.817 ± 0.511	4.490 ± 0.316
SW-18	6.547 ± 0.304	6.682 ± 0.288	6.285 ± 0.388	3.207 ± 0.276
SW-22	21.994 ± 1.307	27.545 ± 0.520	21.114 ± 1.672	13.222 ± 0.499
SW-30A	12.286 ± 0.519	10.183 ± 0.370	11.795 ± 0.664	4.888 ± 0.355
SCS-2	10.605 ± 0.453	11.933 ± 0.363	10.181 ± 0.580	5.728 ± 0.348
SCS-3/4D	16.355 ± 0.665	17.562 ± 0.457	15.701 ± 0.851	8.430 ± 0.439
SCS-5	14.572 ± 0.606	14.605 ± 0.428	13.989 ± 0.775	7.010 ± 0.411
NAB-9	11.312 ± 0.704	11.841 ± 0.349	10.859 ± 0.902	5.684 ± 0.335
Minimum	4.369 ± 0.226	1.133 ± 0.520	4.194 ± 0.289	0.544 ± 0.290
Maximum	21.994 ± 1.307	27.545 ± 0.520	21.114 ± 1.672	13.222 ± 0.499
Mean±StDev	11.280 ± 4.301	10.545 ± 6.357	10.829 ± 4.130	5.062 ± 3.051

Table 2. Comparison of Soil with other Studies.

Country	Sampling location	Measurement technique	Concentration, Bq/m^{-3}		Ratio	Reference
			Rn-222	Rn-220	Rn-220/Rn-222	
Ghana	G.Mine	HPGe	4,194 - 21,114	544 -13,222	0.444	This study
Ghana	G.Mine	Alpha Guard	56-268	-	-	Andam and Amoo, 1994
Ghana	Mine	Alpha Guard	43-878	-	-	Andam and Amoo, 1994
Ghana	Mine	HPGe	12,500-41,300	-	-	Faanu, 2011
Ghana	Fault	-	9,910 - 42,10	-	-	Amponsah, 2008
Turkey	Geotherm. Area	SSNTD	98 - 8594	-	-	Tabar et al., 2013
Italy	Volcanic Mt	RAD7 radon meter	232-104,300	10-23,350	0.503	Giammanco et al., 2007
India	-	RAD7 radon meter	3,200-17,200	-	-	Mehra et al., 2015
India	*Dwellings	SSNTD	-	-	0.503	Ramachandran, 2010
Russia	-	-	1,700 - 24,000	-	-	Iakovleva and Ryzhakova, 2003
Sudan	soil	SSNTD	5,500 -15,100	-	-	Elmoniem and Elzain, 2015

G.: Gold Mt.:Mountain SSNTD: Solid State Nuclear Track Detector *Indoor thoron and radon

69.880 Bq/Kg with mean value of 37.527 ± 15.508 Bq/Kg compared to the global limit of 370 Bq/Kg. The value for H_{in} ranged from 0.065 to 0.248 Bq/Kg with a mean value of 0.132 ± 0.053 Bq/Kg which is lower than the accepted value of the unity. While for total annual effective dose due to external and internal gamma dose the range was 0.060 to 0.175 $mSvy^{-1}$ with the mean value of 0.11 ± 0.025 $mSvy^{-1}$ against the world value of 1 $mSvy^{-1}$. Comparison of Ra_{eq}, H_{in}, H_{ex}, and AED with the other studies in Ghana and elsewhere was made and Figure 7 clearly shows that values of Ra_{eq}, H_{in}, H_{ex} and AED obtained are much lower than those recommended values of 370, 1, 1, 1 Bq/Kg, respectively by UNSCEAR (2008).Figure 7 also shows that the concentration of Ra-226, Th-232, K-40 in this study are lower than the global values of 37, 33, 400 Bq/Kg, respectively.

Conclusion

Studies at Newmont-Akyem, was carried out using

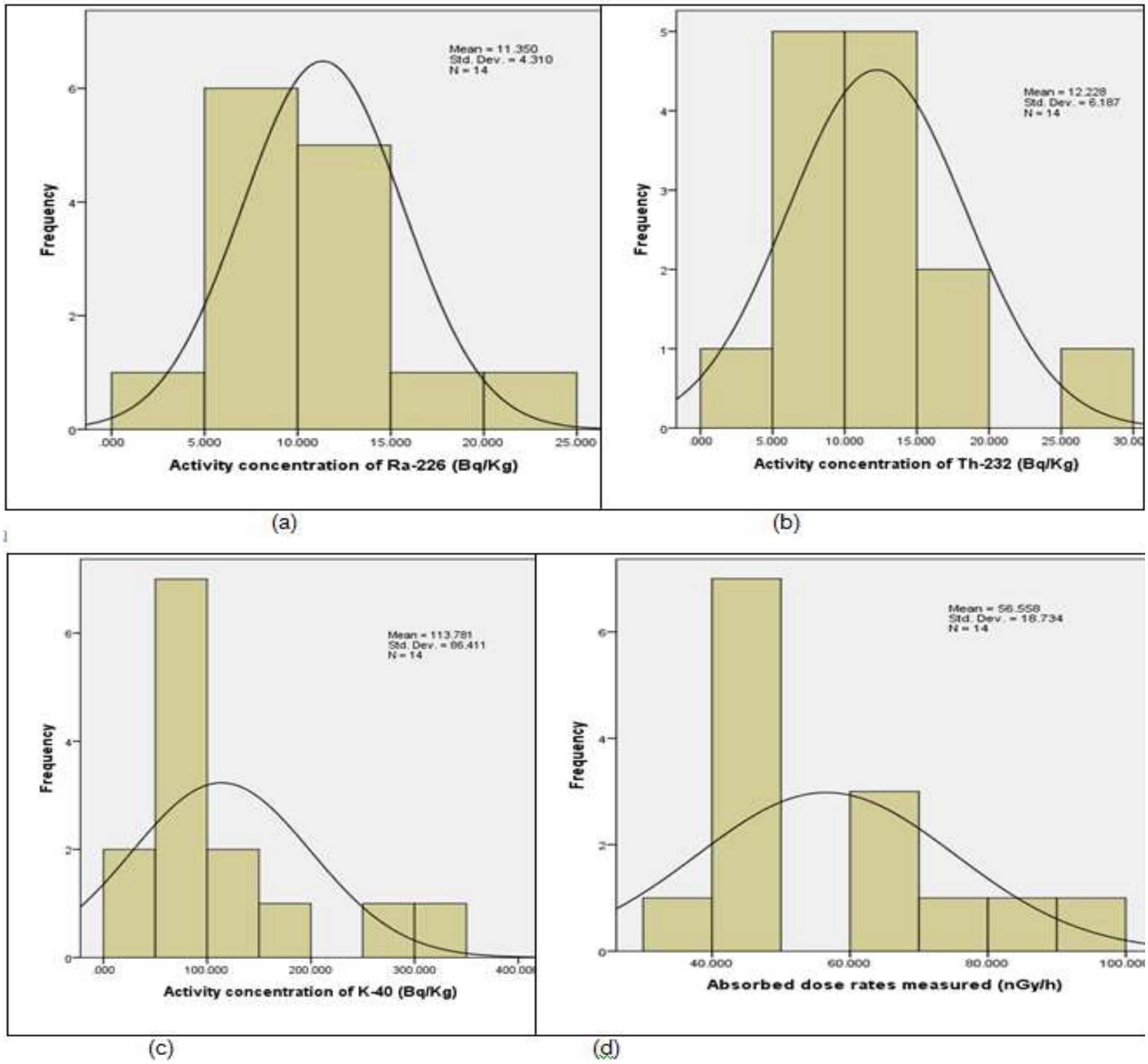

Figure 6. (a) Frequency distribution of ^{226}Ra. (b) Frequency distribution of ^{232}Th. (c) Frequency distribution of ^{40}K. (d) Frequency distribution of the measured absorbed dose rates in the field.

Gamma Spectrometry System equipped with High Purity Germanium detector. The samples were analyzed in order to assess the dose and hazards due to ^{226}Ra, ^{228}Ra, ^{232}Th, ^{40}K, ^{222}Rn and ^{220}Rn. The soil gas radon concentration correlated with that of radium showing that, radium is the source of soil gas radon. The study has shown that the annual effective dose due to ^{226}Ra, ^{232}Th, ^{40}K is lower than the world averages.

Although, soil gas radon and thoron concentrations were calculated, it was difficult to find AED based on soil gas radon and thoron as literature indicates that it gives limited results. Therefore it would still be recommended to conduct direct measurement of indoor radon and thoron and compare the results. Thus, it is very difficult to conclude whether people at Akyem are safe from radon without AED based on ambient radon and thoron. However the results for soil gas radon have shown that, the people may safely use the soil with very minimal

Table 3. Annual effective dose, Radium Equivalent Index (Ra_{eq}), internal and EXTERNAL harzard indices (H_{in}, H_{ex}) of soil samples.

Sample location	Concentration, $BqKg^{-1}$			AED, $mSvy^{-1}$		
	Raeq	Hin	Hex	External	Internal	Σ_{AED}*(ext,int)*
AFO-12	22.633 ± 1.664	0.086 ± 0.006	0.061 ± 0.004	0.025 ±0.0019	0.038 ± 0.0028	0.063 ± 0.003
SW-2A	31.851 ± 2.112	0.120 ± 0.007	0.086 ± 0.006	0.036 ±0.0024	0.053 ± 0.0036	0.089 ±0.004
SW-3	26.623 ± 1.628	0.097 ± 0.005	0.072 ± 0.004	0.031 ±0.0018	0.046 ± 0.0028	0.077 ± 0.003
SW-4	30.395 ± 1.807	0.108 ± 0.006	0.082 ± 0.005	0.035 ± 0.0021	0.053 ± 0.0031	0.088 ± 0.003
SW-11	32.051 ± 2.077	0.113 ± 0.007	0.087 ± 0.006	0.038 ± 0.0023	0.056 ± 0.0035	0.094 ± 0.004
SW-15	19.708 ± 1.092	0.065 ± 0.004	0.053 ± 0.003	0.024 ± 0.0013	0.036 ± 0.0019	0.06 ± 0.002
SW-17	30.380 ± 1.857	0.107 ± 0.006	0.082 ± 0.005	0.035 ± 0.0021	0.053 ± 0.0032	0.088 ± 0.003
SW-18	24.384 ± 1.498	0.084 ± 0.005	0.066 ± 0.004	0.029 ± 0.0017	0.043 ± 0.0026	0.072 ± 0.003
SW-22	69.880 ± 4.889	0.248 ± 0.017	0.189 ± 0.013	0.058 ±0.0055	0.087 ± 0.0082	0.145 ± 0.008
SW-30A	51.271 ± 2.407	0.172 ± 0.008	0.138 ± 0.007	0.069 ± 0.0046	0.103 ± 0.0070	0.172 ± 0.007
SCS-2	36.028 ± 2.136	0.126 ± 0.007	0.097 ± 0.006	0.061 ± 0.0027	0.091 ± 0.0041	0.152 ± 0.004
SCS-3/4D	55.948 ± 3.260	0.195 ± 0.011	0.151 ± 0.009	0.048 ± 0.0026	0.072 ± 0.0040	0.12 ± 0.004
SCS-5	60.720 ± 3.034	0.203 ± 0.010	0.164 ± 0.008	0.063 ± 0.0036	0.095 ± 0.0055	0.158 ± 0.006
NAB-9	33.501 ± 2.403	0.121 ± 0.008	0.090 ± 0.006	0.070 ±0.0013	0.105 ± 0.0054	0.175 ± 0.005
Minimum	19.708 ± 1.092	0.065 ± 0.004	0.053 ± 0.003-	0.024 ± 0.0013	0.036 ± 0.0019	0.06 ± 0.002
Maximum	69.880 ± 4.889	0.248 ± 0.017	0.189 ± 0.013	0.070 ± 0.0013	0.105 ± 0.0054	0.175 ± 0.005
Mean ± StDev	37.527 ± 15.508	0.132 ± 0.053	0.101 ± 0.042	0.044 ± 0.0170	0.066 ± 0.0248	0.11 ± 0.025

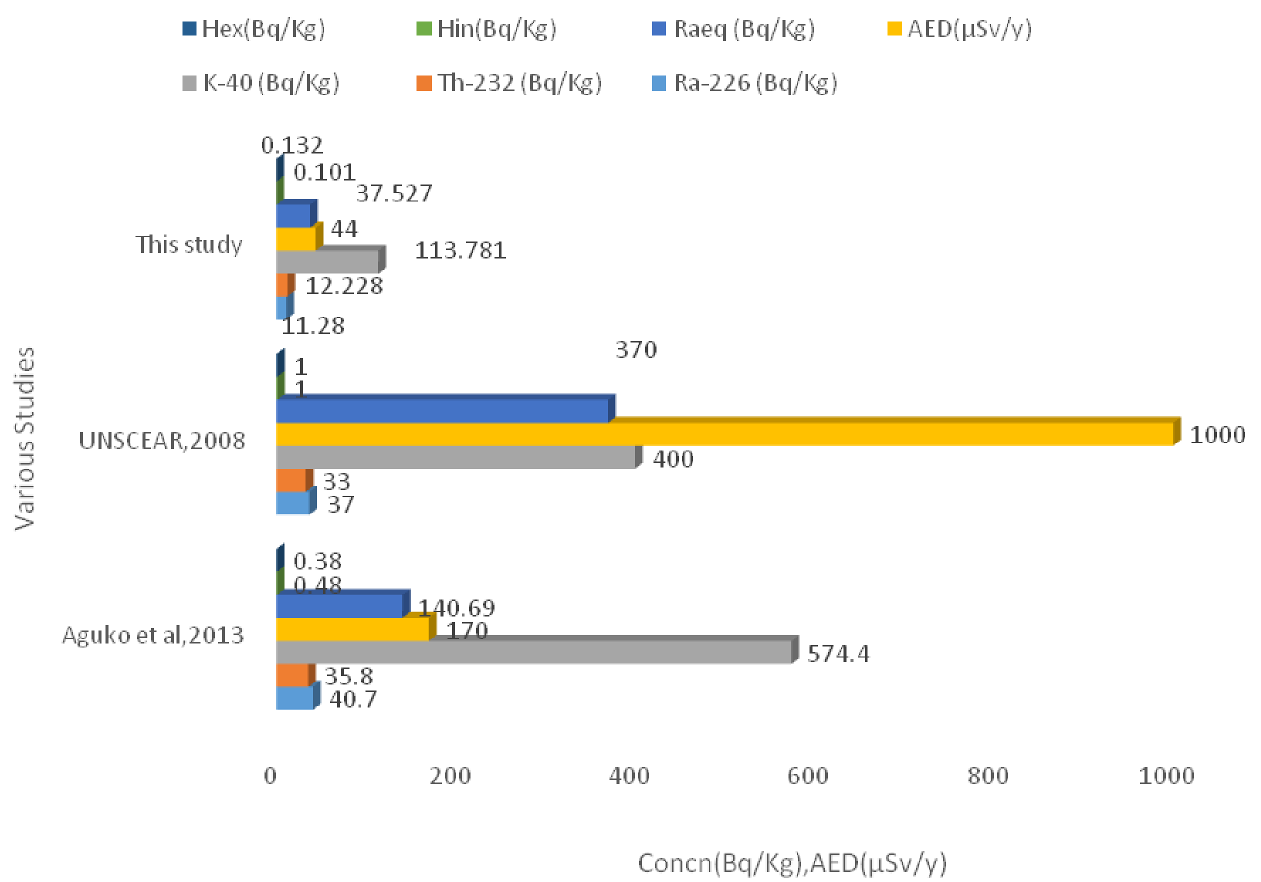

Figure 7. Ra_{eq}, H_{in}, H_{ex}, AED of NORMs compared to the world average values.

radiological risks.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Full Length Research Paper

Coupling chemical coagulation and photodegradation on titaniferous sand for the treatment of tobacco effluents

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Over the last decades, the world production of cigarettes has increased considerably. However, the industrial production generates large quantities of colloidal effluents consisting of toxic and recalcitrant compounds. Thus, taking account the colloidal aspect of the effluent and the persistence of some compounds, this study aims at coupling chemical coagulation and photodegradation on titaniferous sand to treat wastewater from a cigarettes plant in Senegal. The chemical coagulation was handled by aluminium sulfate. The optimal conditions of this chemical process were found at a pH of 7 and a coagulant concentration of 350.4 mg/L. In these conditions, the elimination rate of the chemical oxygen demand (COD) and suspended materials (SM) were respectively 51.32 and 76.92%. Despite its good performances, the chemical coagulation only did not come up with a standard effluent discharge. That is why the photodegradation was conducted to complete the treatment. With a maximum titaniferous sand concentration of 320 g/L, the results highlighted a COD elimination rate of 60% at an initial concentration of 240 mg/L. The COD elimination rate was highly enhanced by increasing the amount of hydrogen peroxide in the system. Indeed, the COD elimination rate was shifted from 61.2 to 72% when the rate of hydrogen peroxide varied from 0.2 to 0.6%.

Key words: Tobacco effluents; chemical coagulation; photodegradation; titaniferous sand.

INTRODUCTION

Tobacco industry is one of the huge companies in the world. China is the greatest producer and consumer of tobacco in the word and contributes to about 40% of the global world production of tobacco (Yi Liu, 2015).

Over the last decades, the world production of tobacco incredibly increased, particularly in developing countries (Novotny, 1999). However, the manufacturing process lead to an important amount of waste which makes

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Figure 1. Sample of titaniferous sand used as photocatalyzer.

tobacco industry as the 18th company which generates more chemical waste (Crini, 2007). More than 200 million tons of wastes were released each year (Jing, 2016; Wang, 2009). In 1992, according to Toxics Release Inventory (TRI) more than 27 million kilograms of waste from USA tobacco companies were generated and only 2.2 million kilograms were treated. These wastes, once discharged into the environment lead to an important ecological issue (Meng, 2014; Zhong, 2010; Zi, 2013). In fact, tobacco effluents include harmful, toxic and recalcitrant compounds. These last one generally come from the decomposition of tobacco sheets which are mainly made of acids (malic, citric, furamic, oxalic, succinic, phenolic, chlorogenic, etc.), quinine and above all nicotine. The elimination of nicotine in wastewater was studied in several works by adsorption (Yurdakoc, 2008; Shin, 2011), and biodegradation (Wang, 2009; Zhong, 2010; Meng, 2010). It should also be noted that tobacco waste water are generally heavily loaded with suspended materials and colloidal particles. However, if photodegradation is required for example to treat these effluents, the colloidal particles would prevent good penetration of the light. Thus, based on the colloidal nature of tobacco liquid effluents, this study focus on the treatment of the tobacco effluents from a plant in Senegal by coupling chemical coagulation and heterogeneous photocatalysis on titaniferous sand. In addition, the use of coagulation as a pretreatment would reduce the turbidity of the effluent, which would allow better excitation of the photocatalyzer. Indeed, no study reporting concerning the coupling between these two techniques to treat tobacco waste water. The chemical coagulation is one of the most useful methods of colloidal particles destabilization. The coupling method with other oxidative, membrane or biological processes was successfully studied in several papers (Rasoola, 2016; Han, 2008; Rodríguez-Chueca, 2016; Amor, 2015; Hashem, 2016).

MATERIALS AND METHODS

The coagulant

Hydrated aluminium sulfate [$Al_2(SO_4)_{3,}18H_2O$] was the coagulant which was used in this study. This coagulant, as white crystals, is made by a French company (LABOSI). For the experimental purposes, a stock solution of pure aluminum sulfate was prepared with a concentration of 60 g/L which means a concentration of 116.8 g/L of the commercial product [Al_2 (SO_4) $_3 18H_2O$].

The titaniferous sand

The used titaniferous sand was from an ore in Senegal. Its black and metallic aspect is as shown in Figure 1. The sand contains 58% titanium dioxide. In addition to titanium dioxide, it contains other dioxides such as: Fe_2O_3, FeO, V_2O_5, Cr_2O_3, SiO_2, Al_2O_3, P_2O_5, MgO, MnO, CaO, etc. The physical and granulometry parameters of this sample are displayed in Table 1.

Method and frequency of effluents sampling

Trials were executed on effluents which were sampled each hour during one week from 7 am to 10 pm. The samples were collected in sterile bottles canned in a freeze at 4°C. By the end of each morning 1.5 L of effluent was sampled according to the flow of collecting hours. A the end of the week, 8 L of effluent was recovered to carry out characterizations in terms of physical and chemical analysis and also experiments of chemical coagulation and photodegradation on titaniferous sand.

Characterization of tobacco effluents

The physical and chemical analyses were handled following the described methods of AFNOR standard for water (Table 2). Aside from the phosphorus content, the pH and the temperature, the analytical results did not conform to the Senegalese standard discharges (NS05-061) for pollutant parameters. In addition to the ratio DCO/DBO_5 which was 2.6 highlighted a recalcitrant pollution.

Method of chemical coagulation

Trials of coagulation-decantation were executed according to the well-known Jar-Test protocol. A serial of agitated recipients was used in an identical way. One of them contained only the effluent (witness solution) and the others contained the same effluent to which were added the increasing doses of coagulant. Reactants were mixed at first quickly during 3 min with a stirring speed of 150 rpm. Then, the agitation was reduced to favor the flocculation. Finally, flakes were left for a rest during 1 h and the results were estimated by measurements of turbidity and SM by a HE9 turbidimeter and filtration device on cellulosic fiberglass (45 mm of diameter and 0.45 µm of porosity).

Method of photodegradation

Trials of photocatalysis were executed in a 250 mL photocatalytical

Table 1. Characteristics of the tinaniferous sand.

Physical and granulometry parameter	Value
Absolute density (kg/m^3)	4054
Related density (kg/m^3)	2500
Porosity (%)	38.33
Specific Surface (g/m^2)	11.84
Effective diameter, D_{10} (mm)	0.100
Average diameter D_{50} (mm)	0.125
D_{60} (mm)	0.130
Coefficient of uniformity, Cu	1.300

Table 2. Characteristics of tobacco effluents.

Parameter	Value
SM (mg/L)	260
COD (mg/L)	1144
BOD_5 (mg/L)	440
N (mg/L)	6.5
P (mg/L)	2.31
pH	6,5
T (°C)	29

batch reactor. The titaniferous sand was suspended in the photodegradable effluent which was agitated and let to the sun during 8 h. The solar database varied from 240 to 707 w/m^2.

The elimination of the effluent organic pollution in time of irradiation was followed by a measurement of the chemical oxygen demand consistent with the ebb method by a "BLOCK DIGEST" multiposts heating system.

RESULTS AND DISCUSSION

Chemical coagulation

Influence of the coagulant

The concentration of coagulant varied from 0 to 525.6 mg/L. Two parameters (turbidity and SM) were measured. The obtained results are displayed in Figure 2.

The results show that the progressive addition of coagulant causes a decrease of the turbidity and the suspension materials until an optimal concentration of 350.4 mg/L where the turbidity and SM reach the minimal values of 10 NTU and 76 mg/L, respectively. This decrease of the parameters of turbidity and SM is due to the fact that the particles of coagulant destabilize colloids negatively charged in the effluent, by neutralizing the charges which generate the strengths of aversion between colloids. Nonetheless, when the coagulant concentration is higher than 350.4 mL, the turbidity and the SM increase. This is explained by the destabilisation phenomenon of colloid particles. Indeed, the availability of their sites decreases and prevents the formation of interparticular bridges. Consequently, the effluent is very charged by coagulant with a bad clarification.

Influence of pH

The initial pH of the pollutant is a key parameter which determines significantly the efficiency of the chemical treatment. So, to better understand the incidence of the pH, a range of wastewater was handled in the optimal concentration of coagulant with an initial pH going from 5 to 8. The evolution of the turbidity and the SM according to the initial pH of effluents after 1 h of coagulation is represented in Figure 3.

It was noticed that the pH of 7 is the optimal value for the elimination of turbudity and SM. These results are consistent with the hypothesis that the optimal value of pH is generally between 6 and 8 for the treatment of organic and colloid compounds with aluminum sulfate (Canizares, 2009; Carrier, 2007). The significant decrease of the turbidity and the SM would be explained by the important affinity between the hydroxyle forms of aluminium and the suspended materials. In addition, at a pH of 7, the soluble forms of aluminium are available.

The results of the effluents treatment by chemical

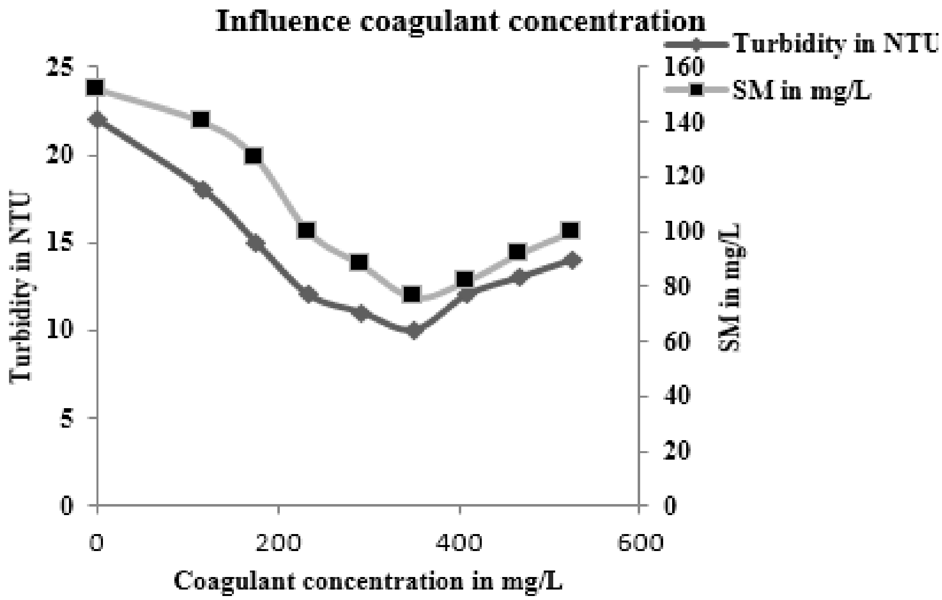

Figure 2. Deduction of turbidity and SM according to the coagulant concentration; V=100 mL; pH=6.5; T=29°C.

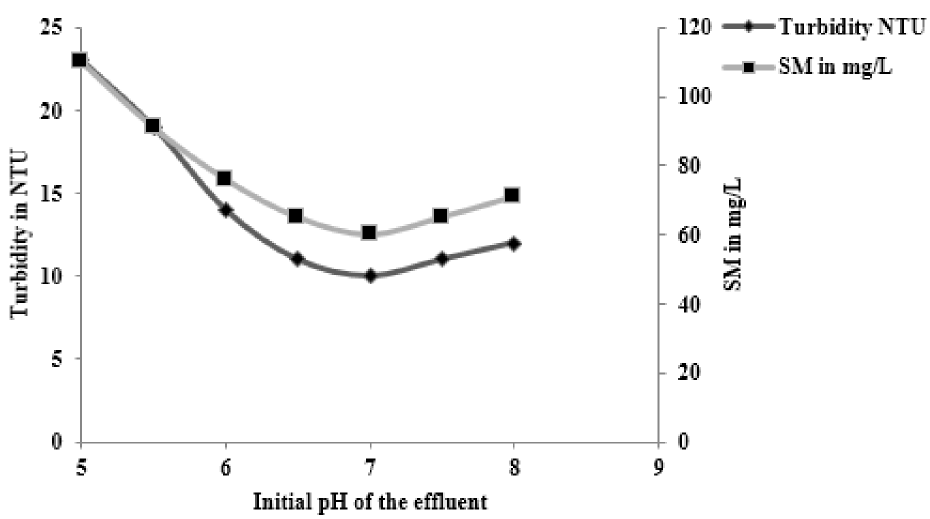

Figure 3. Deduction of turbidity and SM according to initial pH of the effluent; V=100 mL; coagulant concentration=350.4 mg/L.

coagulation in the optimal conditions of coagulant concentration and pH are displayed in Table 3. Only the chemical oxygen demand (COD) and suspended materials (SM) were monitored as measurement parameters.

Results show that in spite of an important deduction of the COD (51.32%) and SM (76.92%), the effluent remains always not corresponding with regard to the standards of landfill. So, the photodegradation on the titaniferous sand was used for a secondary treatment.

Photodegradation on titaniferous sand

Influence of the pollutant initial concentration

In order to study the impact of the initial concentration of the pollutant, trials were working out on two samples

Table 3. Characteristics of effluents after coagulation and decantation.

Parameter	Before coagulation	After coagulation	NS05-061 standard
COD (mg/L)	1144	556.8	200
SM (mg/L)	260	60	50

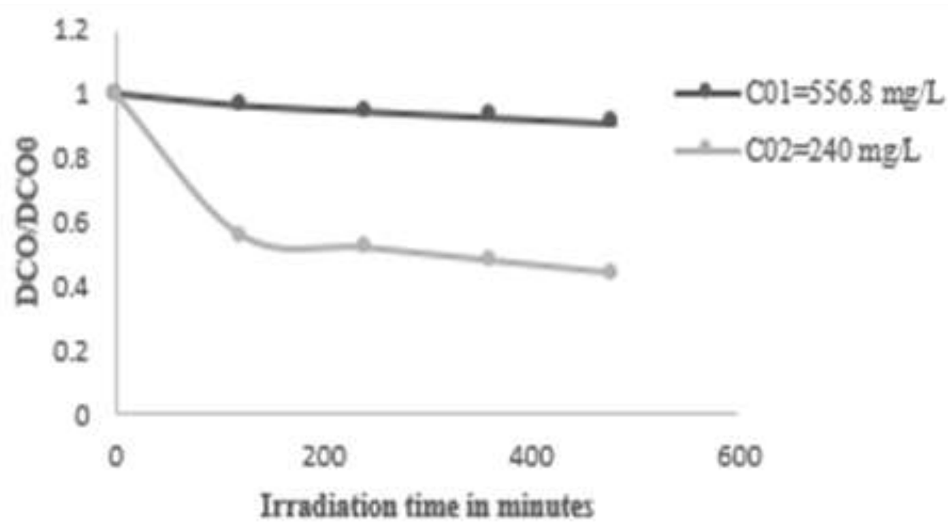

Figure 4. Evolution of the residual fraction of COD at a fixed mass of catalyst according to the time of irradiation; M_{STF} = 70 g; V = 250 mL; pH = 6.

C_{01}=556.8 mg/L and C_{02}=240 mg/L. The first one was obtained by chemical coagulation and the second one by dilution of the first sample. The concentration of the titaniferous sand was maintained at 280 g/L. Figure 4 shows the evolution of the residual fraction of the COD according to the time of irradiation.

The results let us to figure out that the catalyst photodegradation of the pollutant is more important in diluted medium and reaches an elimination rate of 56%. In fact, at low concentration, the number of adsorption sites is higher than the number of pollutant molecules per volume. At high concentration, the catalyzer is saturated, consequently, it decreases the probability of meeting between an available active site and molecules of pollutants.

Influence of the titaniferous sand mass (M_{STF})

To optimize the amount of catalyzer for the degradation of the effluent, masses of 50 to 100 g were used in a volume of 250 mL at a pH of 6. The obtained results are displayed in Figure 5.

In the concentration range which was studied, it was noticed that the mass of catalyzer impacted the rate of pollutants degradation. Indeed, for a mass of 80 g and after an irradiation time of 480 mn, 60% of the initial COD were degraded. It constitutes an optimal value for the photodegradation. Elsewhere, when the mass of catalyzer is lower than 80 g, the deduction of the COD is less than 60%.

Generally, the increase of the catalyzer concentration favors the adsorption of the pollutant on the surface, what enhances degradation velocity. However, a high catalyzer concentration affects the distribution of the light in the solution thus the velocity of degradation decreases (BECHEIKH, 2012).

Influence of the hydrogen peroxide

The most studied inorganic oxidizer for its positive effect on the kinetics of photodegradation is doubtless the hydrogen peroxide. So, further to the study of the effluent

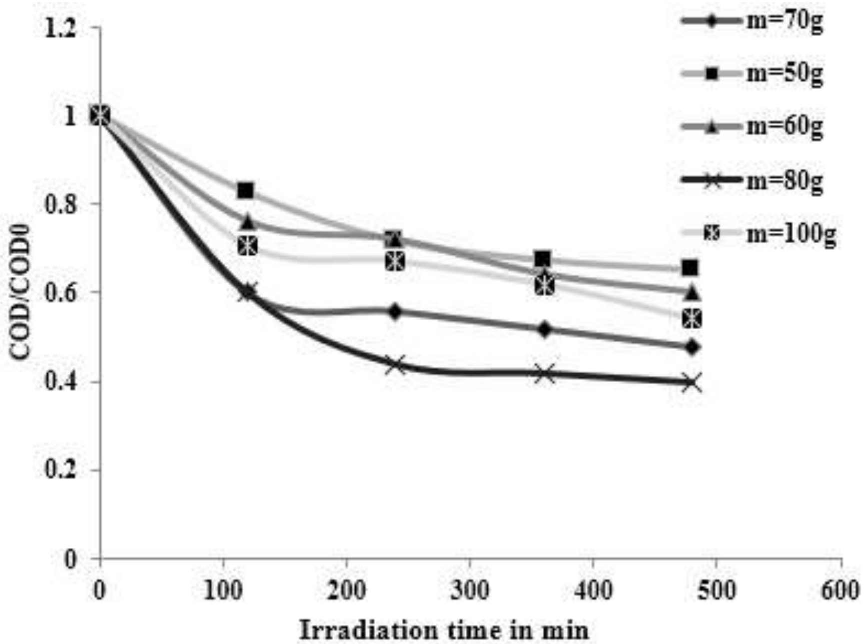

Figure 5. Evolution of residual fraction of COD at different masses of catalyst according to the time of irradiation; V=250 mL; C_0=240 mg/L; pH=6.

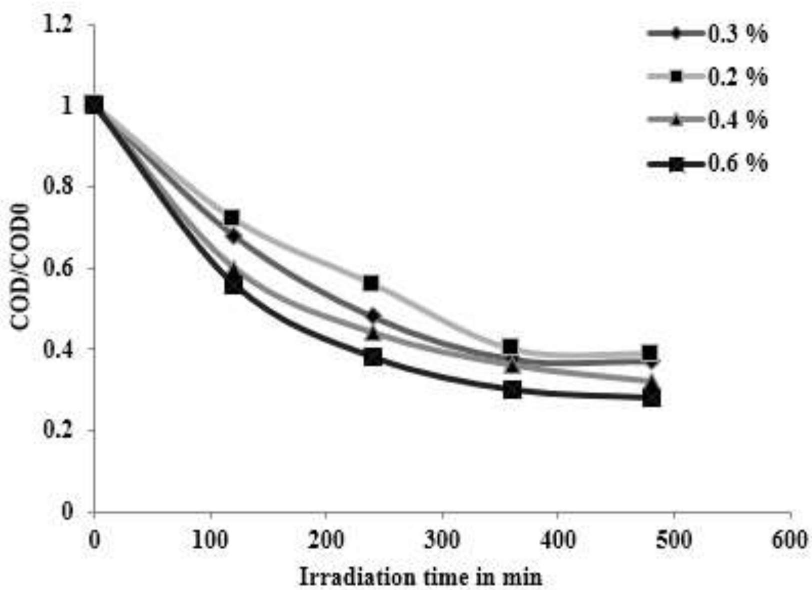

Figure 6. Evolution of the residual fraction of COD at different H_2O_2 contents according to the time of irradiation; M_{STF} = 80 g; V=250 mL; COD_0=240 mg/L; pH=6.

initial concentration and the charge of catalyst, the influence that can have the hydrogen peroxide on the kinetics of degradation of pollutants was tested. For that purpose, trials were executed with samples from 0.2 to 0.6% of hydrogen peroxide content by fixing the concentration of the sand to 320 g/L (320 g of titaniferous sand per liter of effluent) and the effluent to 240 mg/L. The Figure 6 gives the evolution of the residual fraction according to the time of irradiation.

The kinetics of the degradation is significantly enhanced by increasing the concentration of hydrogen peroxide. In fact, the deduction of the effluent COD was shifted from 61.2 to 72% when the rate of hydrogen peroxide varied from 0.2 to 0.6% after 480 min of irradiation. This could be explained by the fact that hydrogen peroxide is an acceptor of electrons which reacts with free electrons being to the band of conduction of the photocatalyst and so prevents them from recombining with holes H^+. Furthermore, the hydrogen peroxide can increase radicals quantity of hydroxyles in the system by a photolytic break.

Conclusion

In this work, waste water from a cigarettes plant was treated in a discontinuous way. This treatment consisted of chemical coagulation by aluminium sulfate and photodegradation on titaniferous sand. The chemical coagulation, as well as sufficient for effluents landfill lead to lowering efficiently the COD to 51.32% (556.8 mg/L of final COD) and the SM to 76.92% (60 mg/L of final SM). Nevertheless, the use of photodegradation on titaniferous sand as secondary treatment of the effluent after chemical coagulation was not very important. Indeed, the elimination rate was 8.62% during 480 min of irradiation. Usually, the Advanced Oxidation Processes (AOP) are not efficient at high concentration of pollutants. A deduction rate of 60% was obtained by working with diluted effluent at a COD of 240 mg/L and a maximum titaniferous sand concentration of 320 g/L. This result was significantly enhanced by the presence of hydrogen peroxide. In fact, the COD elimination rate was shifted from 61.2 to 72% when the rate of hydrogen peroxide varied from 0.2 to 0.6%.

However, it would be very important to have an idea about degradation products and also to doper the titaniferous sand. Indeed, doping of TiO_2 would allow mineralization at reasonable times. Moreover, the efficient use of photons in the ultraviolet represents only 5% of the sunlight.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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