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African Journal of Environmental Science and Technology

Full Length Research Paper

Vulnerability of agro-pastoral farms to climate change in Dakoro

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In Niger, climate change affects the majority of the population, especially the rural communities. The present study intends to contribute to the understanding of the actual perception of climate changes by the population along with the degree of apprehensiveness of the population regarding the climatic manifestations described by scientists. To this end, two communities have been targeted in the Department of Dakoro. The data from the study were mainly obtained by collecting quantitative and qualitative information on the community perception of the impacts of climate change and variability. The results of this scientific contribution demonstrate once again the link between the experiences of producers and scientific evidence. Thus, perceptions of the phenomenon of climate change are very diverse and vary according to the communities and their level of vulnerability. The impacts listed include drought, rainfall deficit, rising temperatures and decreasing soil fertility. The rainfall deficit associated with the decline in soil fertility and the resurgence of crop pests weakens the agricultural sector. The livestock system is highly vulnerable to recurring forage deficit, drought, and degradation of grazing areas and, above all, animal theft, which reflects the increased poverty in the area. Further research on the characterization of adaptation strategies to the impacts experienced by producers will be appropriate.

Key words: Vulnerability, climate change, agro-pastoral, Dakoro.

INTRODUCTION

The earth has always experienced climatic fluctuations per cycle of global warming and cooling. Thus, through

the Intergovernmental Panel on Climate Change (IPCC / IPCC) assessment report, the influence of anthropogenic

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actions on climate variability has improved, and it confirms that, human actions have led to global warming (IPCC, 2007). Climate change and variability are real threats to people in developing countries. It has therefore been recognized that Africa in general and the Sahel countries in particular are among the areas most vulnerable to the effects of climate change (CRA, 2009). This vulnerability can be explained by the strong dependence of the economies of these countries on activities sensitive to climate change which otherwise will suffer because of their weak technical, institutional and financial capacities.

Niger with an area of 1 267 000 km², one of the largest countries in West Africa, due to its enclavement and its very variable climate, suffers the full impact of variability and climate change (CRA, 2009). In recent decades, Niger has recorded agricultural and fodder production every three years below the needs of the population, with successively -20 kg / inhabitant in 2000 to 2001, -40 kg / inhabitant in 2004 to 2005 and -28 kg / inhabitant in 2009 to 2010.

In Niger, climate change affects the majority of the population, especially the rural communities. In this sense, in 1995, the country launched the process of drafting and adopting a national environment plan following the Rio de Janeiro Summit, its Initial National Communication (CNI) as well as its National Strategy and Plan of Action on Climatic Change and Variability (SNPA/CVC) in 2003. Niger subsequently elaborated and submitted for funding, in accordance with the Marrakesh accords and the National Adaptation Program of Action (NAPA), which aims to contribute to the transfer of technologies for both mitigation and adaptation to climate change priority needs and needs of the country, which deals with the adverse effects of climate change on vulnerable populations in the perspective of sustainable development (SE/PNEDD, 2008). In a report by NAPA (2006), it is clear that the Department of Dakoro, our study area, is among the areas vulnerable to climate variability and change in Niger. Indeed, SIFEE (2009) reports that the agropastoral systems of the Department of Dakoro were experiencing a progressive degradation of the ecosystems (Tarka Valley).

The present study on the vulnerability of producers in Dakoro describes local perceptions and the adaptation of producers to the impacts of climate change. The document is structured around three main points: the first deals with the conceptual framework in which we expose the problem and review some policies on climate change. First is a brief summary of the study area and data collection methods and tools. The second presents the results referring to peasant perceptions of the impacts of climate change. In this part of the analysis, we first analyze natural factors of vulnerability to climate change and then discuss the socio-economic vulnerability

characteristics of the localities studied.

MATERIALS AND METHODS

Study area

Dakoro Department is located in the Northern part of Maradi region of Niger. It covers an area of approximately 12670 km² and borders Bermo Department in the North, Guidan Roumdji Department in the south, Agadez region in the east and Tahoua region in the west. According to the 2012 population census, the department has an estimated population of 631,429 with an average annual growth rate of 4.1% (INS, 2013). This population is predominantly composed of Hausa, Tuareg and Peulhs (Figure 1).

The department of Dakoro is classified among the departments with high climate vulnerability (Tsemogo, 2012). Dakoro Agropastoral ecosystems are experiencing progressive degradation due to both natural and man-made factors. The gradual leaching of agricultural soils and wind activities expose them to the silting phenomenon (SIFEE, 2009).

Data collection

Two communes were targeted in the department of Dakoro for the conduct of this study. The data from the study were mainly obtained by collecting quantitative and qualitative information on the community perception of new agricultural practices and strategies adopted to address the impacts of climate change.

Sampling

To determine the sample, we used various criteria (age, sex, household membership, level of vulnerability, etc.). A total of 258 producers were surveyed, including 165 from Azagor and 93 from Bader Goula.

The study took into account the age aspect with 178 respondents who are under 50 years and 80 who were over 50 years. Given the inequality in enrollment between male and female heads of households and gender mainstreaming, the vast majority of respondents, that is 194 men were compared with 64 women. Social categorization was based on four criteria of vulnerability (availability of land, socio economic activities, cultural values, livestock capital, family burden) pre-established by the population with the support of the Adaptation Learning Program (ALP) project: A (Vulnerable), B (Moderately vulnerable), C (Very vulnerable) and D (Extremely vulnerable) (Tsemogo, 2012; Care International, 2010). Thus, the sample included 90 extremely vulnerable household heads, 77 highly vulnerable households, 52 heads of moderately vulnerable households and 39 vulnerable households.

As for the occupational categories, the choice was random. It should be noted, however, that the focus has not been selective, so no distinction of age or social category has been made. This means that the choice of our sample fits perfectly into the dynamics of a combination with the probabilistic method. It is basically trying to put in place new causes to observe new realities.

Collection tools

The tools used in this study were individual questionnaires, focus groups, problem trees and interviews with technical services, CSOs / NGOs working in the field. These tools were validated after several meetings with the project team members to clarify the

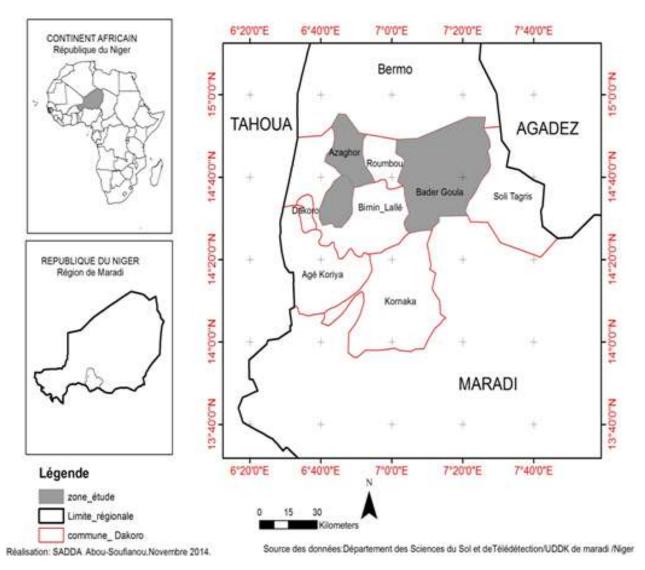


Figure 1. Map of Dakoro Department showing target communes.

different points and allow their good administration to get the target populations. A preliminary evaluation of the tools in a community was mainly aimed at judging the relevance and feasibility of the various guides at the end of which several points were readjusted and refined. The data collection tools were developed on the basis of several indicators. These indicators relate in part to the socio-economic situation of the respondent. A distinction has been made between the number and duration of seasons today as compared to 20 years ago. Through this comparison, the dynamics of impacts on the various environmental components (air, soil, water, animal and plant species, household economies, social relations) between the two periods are identified.

In each community focus groups, women and men were facilitated with 8 to 10 people per focus. In total, a total of 16 focus groups were carried out. This initial work allows to enrich and to diversify the quality of the answers, to arrive at a finer analysis of the results. The problem tree was administered from the focus group to highlight the vulnerability of the breeding system.

Data processing and analysis

After the data collection in the field, we analyzed the various tools. Two types of analyzes were used to exploit this data collected using the SPSS 16.0 software. The variables analyzed are producer perceptions and producers' vulnerability indicators supported by direct evidence and observations, to confirm these perceptions. Basically, these different analyzes have highlighted the illustrations and the diversity of the testimonies of the populations encountered. Descriptive statistics conducted in Microsoft excel 2010 were used to summarize the data.

RESULTS AND DISCUSSION

Producer vulnerability

Vulnerability is not limited to the manifestation of a level of

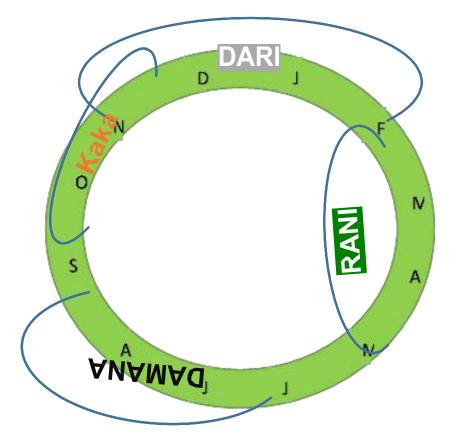


Figure 2. Seasonal calendar.

poverty, it is multifaceted. It varies according to the socioeconomic and agro-ecological characteristics of agricultural holdings. The results of the study allowed us to identify four (4) dimensions of vulnerability:

1. Environmental dimension of agro-pastoralist vulnerability

In Dakoro Department, more than 90% of climate vulnerability factors are caused by natural phenomenon: rainfall deficit, increase in temperature, drought and the frequency of lime and violent winds. The analysis of the peasant perception of diversity and the evolution of seasonal variability has revealed a profound change in the length of the seasons. In all communes of Dakoro, the agricultural calendar is divided on four major seasons: dry or "Rani", harvest or "Kaka", winter or "Dari" and rainy or "Damana" season. This result support the data of Lawali (2011) obtained in Tchadoua (Maradi) department (Figure 2).

(a) Dari: Commonly known as the cold and dry season, which extends from November to February, this season

is characterized by low temperatures, conditions favorable to the practice of irrigated crops.

- (b) Rani: Period from the end of the cold season (February) to the arrival of the first rainy days (June) is marked by high temperatures up to 42°C. This is the period during which exodant go to urban centers.
- (c) Damana: This season extends from the beginning of the first rains (June) to the harvest period (September), it is the rainy season.
- (d) Kaka: This is a short period between the rainy season and the beginning of the cold season, commonly known as the harvest period. It is characterized by an abundance of food and pasture; in this sense, there are widespread damage caused by several conflicts between farmers and breeders.

In terms of climate change, more than 90% of household heads have extended the length of the warm season, while the rainy season is shortening its duration. According to the respondents, winter appears to be unchanged except there is a discrepancy and sharp decrease in excessively low temperatures in Dakoro area (Figure 3).

Analysis shows that rainfall is no longer regular in time

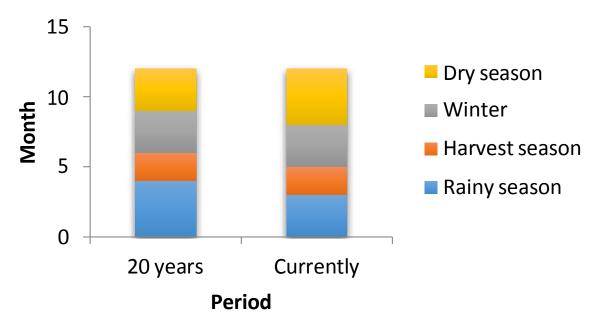


Figure 3. Variation of the duration of the seasons over a period of 20 years.

and space. The rains that began between May and June are now recorded in the second half of July at the beginning of August. In Bader Goula, during the winter season the first rains were recorded in June and spread out until September. At the same time in Marafa (Azagor commune), the first rains fell only in late August and intense rains were recorded in September and October.

Moreover, in most of the areas, the first rains were recorded in April and extended until October, but almost half of the rainfall rains fell in August (197.5 mm in 12 days). The periods of intense heat are characterized by maximum temperatures of up to 50°C in the months of March and April. As a result, 80% of respondents recall that during the dry and cold season, low temperatures occasioned a circle around the fire to warm up and nowadays temperatures are no longer freezing. Thus, result confirms that Tsemogo (2012) describes the shortening of the rainy season that the populations perceive in Dan Sarko comunes (Dakoro). These results are also, similar to the study of Mkoka (2008), which explains that in recent years in Malawi, the seasons have lost their regularity in almost all regions of the country. Rainfall is sometimes one month late or stops early.

What are the consequences of the seasonal variation on the production potential? On the edaphic plane, the perceptions of the producers reveal a multitude of natural and anthropic causes (Figure 3), which contribute to the decline of fertility. The soil has suffered the most dramatic decline in fertility for 20 years, moving from "very fertile" to a "non-fertile" state as a farmer puts it:

"Before we did not plow more than twice. Another farmer supports this opinion. According to him:" as soon as we sowed, we went to pasture and returned only to reap the good production, this is no longer the case."

Thus, excessive logging and inadequate rainfall coupled with overexploitation of agricultural land has led to a significant reduction in yields. Deficient irrigation subjects the crop to water stress, sometimes throughout the period of decline, which can cause a drop in yield (Mkoka, 2008). In Dakoro, this drop in yield led more than half of the farmers to abandon the maize crop in view of its demand for water and nutrients through the use of fertilizers. A study found that the 2012 drought in the US Midwest reduced the expected maize crop by 25%.

Cultures are also attacked by crop pests that appear to be related to climatic variability and the appearance or disappearance of certain crop pests such as *Gerbillus nigériaen*, *Heliocheilus albipunctella*, *Pachnoda interrupta*, *Passer luteus* and *Quelea quelea*. Farmers' perceptions and expertise allow them to assume that, higher temperatures will increase the fertility and growth rate of insect pests and the frequency of epidemics. These perceptions support IFRI's (2009) research which indicates that higher temperatures reduce crop yields while causing weed and parasite proliferation.

2. Early drainage of water points

Another element of producer vulnerability is the scarcity of water. The depth of the water table varied between 20

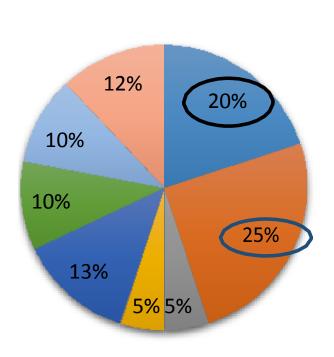


Figure 4. Causes of declining soil fertility.

and 80 m. The amount of recharge of the wells depends on the precipitation recorded. The spatio-temporal irregularity of precipitation causes a lowering of the water table. Water, a free-access resource becomes the object of speculation and monetarization in the pastoral zone. In addition, all these water resources are threatened with silting and / or rapid drying which modify their regime.

Climatic variability and floristic distribution: Climate change has had a real impact on the floristic distribution. Many species have disappeared and the landscape is completely transformed, as one of the interviewed farmer pointed out: "When we were little, we dared not go more than 100 m from the dwellings without soliciting the company of an older brother because the trees were less than 50 m from the huts and stretched as far as the eye could see. Then, one could count more than 400 trees per hectare unlike today that one can see a village from more than 1 km away". Figure 5 describes species that have disappeared over the years.

Species sensitive to the impacts of climate change are severely affected because they do not tolerate rainfall deficit and decrease soil fertility. Thus, species such as *Hyphaene thebaica*, *Schlerocarya birrea* and *Commiphora africana* are threatened with extinction in the Dakoro area). These species are considered by villagers to be the most sensitive to the impacts of climate

reduction of wood through abusive cutting

insufficient rainfall

floods

strong winds

population growth

■ intense plowing

anarchic clearing causing the appearance of crusts

invasive plants

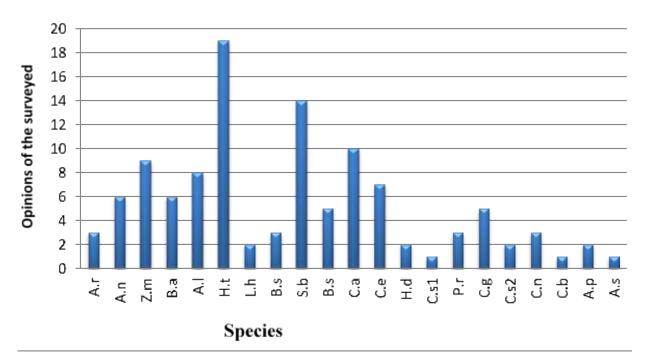
change because they cannot tolerate rainfall deficit and decrease soil fertility (Figure 4).

This perception supports the research of the clearing house of information on biodiversity in Niger, which in 2008 already listed the latter as a species threatened with extinction. Acacia senegal, Cenchrus biflorus, and Hyparrhenia dissoluta are highly endangered. The few remaining samples are resistant to rainfall deficit, degraded soil and, above all, anthropogenic activity in the south of the department, whereas they are almost non-existent towards the north.

3. Socioeconomics dimension of the vulnerability of agro-pastoral farms

In terms of population distribution, the Nation Statistic Indices (NSI) surveys (2013) point out that the Dakoro Department has the highest human concentration of about 18% in the Maradi region. With a population of 5565 and 68,203 inhabitants, respectively in Azagor and Bader Goula, the population pyramid of these districts has a narrowed structure and a gender imbalance with a high proportion of women and young people. Demographic pressure is identified as a pressing factor in the basic livelihoods of agro-pastoralists.

Polygamy is one of the primary drivers of the rising demography in these countries, and majority of the



A.r: Acacia radiana

A.n: Acacia nilotica var adensoinia

Z.m: Ziziphus mauritiana B.a: Balanites aegyptiaca

A.l: Acacia laeta

H.t: Hyphaene thébaica L.h: Leptadenia hastata

P.r: Piliostigma reticulatum

C.s2: Cassia singueana

A.p: Andropogon pseudapricus

Figure 5. Species that disappeared in the study area.

C.a: Commiphora africana H.d: Hyparrhenia dissoluta

C.e:Ctenium elegans

C.n: Combretum nicranthum

S.b: Sclérocarya birrea C.b: Cenchrus biflorus B.s: Boscia salicifolia

C.g: Combretum glutinusum

A.s: Acacia senegal

C.s1: Cymbopogon schoenanthus

producers (89%) belong to the socio-ethnic group Hausa. With two, three or even four wives, polygamy thus accentuates the maternity of women in view that each cowife aspires to have the most heirs who must possess a subsistence capital. This leads to the division of land so that each heir can benefit from an agricultural operation. The land is no longer left fallow because of land saturation to meet ever-demanding needs.

4. Ceremonial practices vulnerability factors

In the Hausa society, traditional ceremonies are usually exorbitantly expensive and often above the means of the household head. Inter and intra-community social relationships influence a strong mobilization of friends and relatives to the ceremony and large attendance means more guests to feed. These obligations sometimes make the host sell his land and / or animals in order to be able to afford the ceremony. The average cost of wedding ceremonies is around 550,000 FCFA, or about 840 €, which is very expensive for a household head who lives on less than one euro a day.

Rural exodus: Vulnerability or adaptation strategy?: Practiced by 15.4% of the producers, the end of the rural works offers the able-bodied men the possibility of migrating towards the receptive zones (Maradi, Nigeria, Libya, Ivory Coast, and Benin), in the quest for greener pastures.

This practice makes the family of the emigrants vulnerable. This is because when the husband goes

away without news or sending money back home, women must be resourceful (Maja-Maja) in order to meet the needs of children. As a result, the entire society becomes more vulnerable to disorderliness.

Discrimination and social: A tiny fringe of the community (5%), in particular the "Black Tuaregs", still admit to living at the mercy of their masters "White Tuareg". The surprising thing is that these black Tuaregs consider this practice as hereditary and dependent on the social system. As a result, slaves do not have access to social benefits such as access to land and livestock. Lack of land / livestock capital coupled with poverty and societal marginality and increases the vulnerability of producers to the impacts of climate variability. Of course, even people living in certain opulence suffer the multifarious effects of vulnerability; these categories nicknamed "the haves" have effective coping mechanisms, which remain the most destructive of the natural ecosystems through their lifestyles. According to a black Tuareg:

"I have no plots of land to cultivate, I just raise my master's animals and carry out all the tasks he requires, and thus I make a living to meet the needs of my family. My children and my wife also work with me and offer the same services to the children and the wife of my master. We are never consulted in the event of decision-making but we are proud of this life because without them life will be difficult for us as they have the money and power".

Fragility of livelihoods: The main economic activities of the communities include agriculture, livestock, trade and crafts. In Azagor, livestock is practiced by 72% of the producers. On the other hand, in the commune of Bader Goula, agriculture is the first economic activity practiced by almost 86% of households. The main crops are millet, sorghum, cowpea and very low groundnut. This agriculture still retains an extensive character, remaining mainly manual using rudimentary tools (for example hilaire and daba).

Moreover, farmers face the problem of selling their products to neighboring markets or to Dakoro due to lack of access, despite low yields due to seasonal variability. Their added value is diminished by the fact that it is the traders who move from terrain to terrain to stock up that make the most profit. These results corroborate with Sabo (2010), which describes the suffering of producers as to the flow of their products of survival. Trade is developed in the municipality of Azagor by lack of market.

Shopkeepers and street vendors buy their goods from the weekly market in Dakoro or in the town of Bader Goula, where commercial activities are intense (practiced by 35% of producers). Even though craftsmanship still retains a rudimentary character, it remains an important income-generating activity, particularly in the community of Makeraoua (Bader Goula commune) where women engage in mat making and pottery.

In recent years, communities have been under recurrent pressure on their livelihoods. 20 years ago, 97% of farmers lived solely on income generated by agriculture. Today, only 69% of producers are self-supporting. Crop yields decreased drastically from 100 boots / ha (1500 kg / ha) 20 years ago to less than 50 boots / ha (750 kg / ha). If this trend continues, less than 20% of the farmers will harvest 50 boots / ha by 2030. 20 years ago, 75% of the cattle farmers managed to meet almost all their needs with proceeds from livestock, this estimated that about 31% of those who manage to meet the few family needs over a period did not exceed 6 months.

Pastoral resources are heavily threatened by overgrazing and advancing on the agricultural front. Indeed, today beyond the northern limit of the crops defined by Law 61-05 of May 21, 1961, there are new fields. The agricultural front has thus reduced pastoralists by 50 km to the north since 1970s (Hammel, 2001). This compromises the proper functioning of livestock farming, which also suffers disruption in its mobility.

Twenty years ago, majority of producers had mixed herds (cattle, sheep, goats, camels, asins, etc.). Nowadays, the phenomenon of sedentarisation of pastoralist communities is being generalized in places, with the creation of villages whose livestock farming is specially oriented towards sheep and goats: almost half of the producers have no cattle or camels. The equines exist only among the chiefs of Peulh or Tuareg villages. Our results have illustrated that sheep, cattle and goats are more affected by the effects of the changes. These animals have a selective diet with fodder in quantity and in appreciable quality and are less resistant to drought, forage deficit which are very sensitive to epizootics. Camels have a coarse diet, usually consisting of aerial fodder.

The mortality rate due to lack of forage has increased from 5 to 20% in 20 years. In fact, the recurrence of climatic sequences and the shift of the rainy season make the most stunted animals vulnerable (Bonnet and Guibert, 2012). Another factor of vulnerability is the theft of animals causing ethnic conflicts. The main perpetrators are the nomads who come to water their cattle at water points, benefiting from the precarious nature of the conditions that nature impose on the victims (Becerra, 2012). The poor distribution of precipitation, the degradation of water quality and the lowering of the water table had already been demonstrated in 1999 in a study by Madiodio et al. (2004) study on "Reducing West Africa's Vulnerability to Climate Impacts on Water Resources, Wetlands and Desertification", points out that

the influence of drought on the acceleration of deforestation and desertification, and by the effect of burnerang in deforestation will accentuate the persistence of the droughts.

Conclusion

The results of this scientific contribution demonstrate once again the link between peasant experiences and scientific evidence. The rainfall deficit associated with the decline in soil fertility and the recrudescence of crop pests weakens the agricultural sector. The livestock system is highly vulnerable to recurrent forage deficits, drought, degradation of grazing areas and, above all, theft of animals, which reflects the increased poverty in the area.

The vulnerability of the two sectors mentioned above (agriculture and livestock farming) is accentuated by the galloping demography, creating new needs to be met and thus new threats to be faced. The research perspectives would identify strategies for adaptation and resilience to these multiple impacts to climate change and variability.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Full Length Research Paper

Spatial and temporal water quality dynamics of Awash River using multivariate statistical techniques

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Awash River has important socio-economic and ecological values in Ethiopia. On the contrary, it is prone to serious water pollution. This study aims to assess the spatial and temporal variation of water quality of the river. Means of the 9 years' (2005-2013) water quality dataset of 19 parameters from 10 stations in the basin were considered. After validating, normalizing and checking the sampling adequacy and internal consistency of the data, principal component analysis was computed and four principal components were generated. Factor loadings, correlations between variables and the principal factors as well as between sites and the principal factors were tabulated. Agglomerative hierarchical clustering done on the dataset resulted in four clusters based on similarity of water quality characteristics. The Mann-Kendall's two tailed trend test detected temporal trends for total hardness in February over all sites and for most parameters in the basin in the 9 years period. Spatial analysis of the 14 sampling sites of the basin showed that as one moves from upper to lower parts of the basin, electrical conductivity, total hardness and chloride decrease in the dry season. However, total hardness slightly increases and total dissolved solids, chloride, and sulfate decrease in the rainy season.

Key words: Agglomerative hierarchical clustering, Ethiopia, Mann Kendall trend, principal component analysis, water pollution.

INTRODUCTION

Surface water quality degradation and its spatial and temporal variation in developing countries like Ethiopia are becoming a threat to ecosystem services due to the rapid increase in population, climate change, industrialization, and the associated land use dynamics in the countries (Kithiia, 2012; Abbaspour, 2011; Davies and Simonovic, 2011). The variation is governed both by natural and anthropogenic factors including climate, types of soils and soil erosion, rocks, hydrology and surfaces through which it moves, agricultural land use, and sewage

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discharge (Bu et al., 2010; Pejman et al., 2009).

Management gap of water quality is observed in Ethiopian River basins as witnessed by poor water quality which does not fit the intended water use requirements (Romilly and Gebremichael, 2011). For instance, the water quality of many rift valley lakes is very poor in terms of salinity and alkalinity and hence not suitable for irrigation, domestic or industrial purposes (HGL and GIRDC, 2009). Investigation of comprehensive and detailed water quality dynamics at a river basin scale has not been done in most parts of Ethiopia. There is also a spatial difference in water quality between the lakes (Tiruneh, 2005; HGL and GIRDC, 2009). In the characterization of the spatial and temporal variability of water quality parameters and sediment distribution in Lake Abava, Gebremariam (2007) came up with a result that water temperature, pH, conductivity, dissolved oxygen (DO), total suspended solids (TSS), and total dissolved solids (TDS) at fixed stations in the lake varied respectively from 21.9 to 30°C; 8.8 to 9.3, 861 to 1162 μScm⁻¹, 5.4 to 7.9 mg.L⁻¹, 4 to 404 mg.L⁻¹, and 618 to 1206 mg.L⁻¹.

Awash River is the most developed water system and hence it is the major component of Ethiopian economy in terms of serving as a water supply source for households, hydropower, industries, small to large-scale irrigation schemes of sugarcane, cotton, fruit, vegetable, and flower farms. Nowadays, there are, however, many factors threatening these advantages of the river, namely, population growth, expansion of irrigated area and deforestation in the upper basin (Taddesse et al., 2004). Moreover, the river receives untreated and uncontrolled domestic, industrial and agricultural wastes from the catchment directly along its course (Belay, 2009; Alemayehu, 2001; Awash Basin Authority [AwBA], 2014). The effect of surface water-groundwater interactions seen in the mixing of Lake Beseka with Awash River could result in quality change (Belay, 2009). Therefore, among the major Ethiopian rivers, these factors have made Awash River most prone to various types of serious pollution.

Consequently, effects of direct waterborne diseases to animals and human-beings and high concentration of heavy metals on vegetables and coliforms were observed. Little Akaki River, which is a tributary of Awash River is unfit for any intended use as it is loaded by high microbiological and chemical pollution. Water pollution in the basin is found to have contributed to the disappearance of aquatic species (Gebre and Rooijen, 2009). The irrigation water heavy metal content is shown to exceed the standard for irrigation water. The incidence of dental and skeletal fluorosis from high concentration of fluoride is well documented in its valleys (Reimann et al., 2003). Though high fluoride concentration is especially apparent in the Rift Valley Lakes basin, the problem is observed to have a negative impact on public health in

the Awash Basin too. Few investigations also showed that nitrate levels are above 10 mg/L in the surface water, and according to Taddese et al. (2003), mean concentrations of heavy metals including manganese, chromium, nickel, lead, arsenic and zinc in Addis Ababa catchments are measurably higher in the soils irrigated by Akaki River (Taddese et al., 2003).

Studies in relation to the spatial and temporal variation in the basin have not been reported so far. However, investigating the spatial and temporal dynamics of Awash River water quality has a scientific and practical significance in that it fills the existing knowledge gap. Therefore, the objective of this study is to investigate the temporal and spatial water quality variation and detect trends of water quality of Awash River.

MATERIALS AND METHODS

Description of the study area

The basin extends from 7°53'N to 12°N and 37°57'E to 43°25'E in Ethiopia as shown in Figure 1. It covers a total land area of 113,304 km² of which 64,000 km² is in western section of the basin. This section of the basin drains to the Awash River or its tributaries. The remaining 49,304 km², most of which comprises the so-called Eastern Catchment drains into a desert area and does not contribute to the Awash River. The Awash River has a total length and an annual flow of 1250 km and 4.6 billion m³ (BCM), respectively. The river originates at an elevation of about 3000 m in the central Ethiopian highlands near Ginchi town about 80 km west of Addis Ababa (Degefu et al., 2013; Tessema, 2011; Berhe et al., 2013).

The main physiographic units of Awash River basin are highlands, the main Ethiopian rift and Afar triangular depression, in which grassland, shrub-land, woodland and forests are the main units. The basin is endowed with several wetlands of various types as well as artificial and natural lakes. It is characterized by wideranging agro-climatic zones with varied ecological conditions. With extreme ranges of topography, vegetation, rainfall, temperature and soils, the basin extends from cold high mountain zones to both semi-desert lowlands (Gedion, 2009). Settled rain-fed agriculture is practiced with possible double cropping in areas receiving considerable spring rainfall (January to May) in addition to main summer rainfall.

Mean annual temperature ranges from 16.7 to 29°C and the mean monthly temperatures range from 9.6°C in the capital to 37°C around Lake Abe Area. Mean annual relative humidity in the basin varies from 60.2 to 49.7%. The mean annual wind speed is 0.9 m/s. The mean annual rainfall varies from about 1600 mm at Ankober to 160 mm at Asayita, according to Berhe et al. (2013). There are two major soil types in the catchment; the deep red clay soil, Nitosol, and the dark clay soil, Vertisol. The Nitosol is found in the upland areas, whereas the Vertisol is found in lowland areas with slopes ranging from 2 to 8% (Moreda, 1999).

The basin has an estimated population of 14.8 million. Majority of this population are engaged in agriculture and animal husbandry. From 48 to 70% of the existing large-scale irrigated agriculture and more than 65% of the national industries are located in the basin (Tessema, 2011; AwBA, 2014). The relative surface water resource of the basin is about 4.65 BCM. It is the most developed and utilized basin since 77.4% of the irrigable land in the basin has been cultivated. Wide varieties of crops are cultivated ranging from

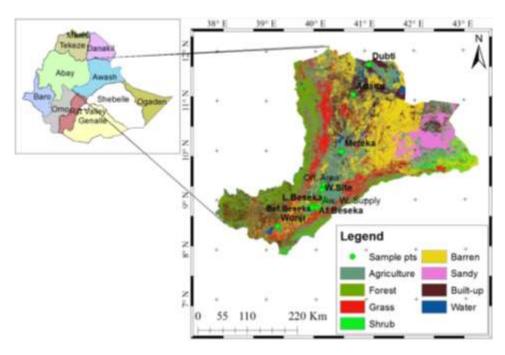


Figure 1. Location map of Awash River Basin with the sampling sites (Based on 2014 LU/LC data).

cereals, vegetables, flowers, cotton to perennial fruit orchards and sugarcane (AwBA, 2014).

Data collection and analysis

Dataset of 10 water quality monitoring stations, containing 19 parameters monitored monthly over 9 years (2005-2013) was collected from AwBA. The water quality parameters considered in this analysis, their abbreviations, their units and methods of analysis (following standard methods for the examination of water and wastewater) are summarized in Table 1 (APHA et al., 1998). The mean of the monthly measured 9-year data-set on the river water quality is summarized in Table 2.

Multivariate statistical techniques and data treatment

Multivariate statistical analysis approaches were used to analyze the water quality data. Such approaches are useful to deal with complex environmental dataset exposed to varying natural and anthropogenic factors and solve the associated problems without misinterpretation. They provide a means of handling large dataset with large number of variables by summarizing the redundancy, as well as reflecting, detecting and quantifying the multivariate nature of ecological data accurately (Hulya and Hayal, 2008; Wang et al., 2007). Principal component analysis (PCA) and cluster analysis (CA) are specifically useful for considering several related random environmental variables simultaneously, and thus for identifying a new, small set of uncorrelated variables that account for a large proportion of the total variance in the original variables (Wang et al., 2007). They were employed here to sort out the variables of water quality parameters and sampling stations.

Cluster analysis (CA)

CA is a multivariate procedure which classifies data based on placing of objects into more or less homogeneous groups. The main idea behind clustering is to combine identical sites as one cluster and group two clusters of the highest similarity as a new cluster, which in turn is combined with another most similar cluster as another new cluster and so on until all clusters become one cluster (Xu et al., 2012). Agglomerative hierarchical clustering (AHC) is the most common and iterative classification method in which clusters are formed sequentially by starting with the most similar pair of objects and forming higher clusters step by step (Singh et al., 2004). AHC was done by Euclidean distance proximity type and Ward's method of agglomeration on the dataset to assess the similarity among sampling sites. The Euclidean distance, which is used to quantify the similarities or differences between the two sites (sampling locations) i and j, was calculated using the formula below:

$$d_{ij}^{2} = \sum_{k=1}^{m} (Z_{i,k} - Z_{j,k})^{2}$$
(1)

where d_{ij} is the Euclidean distance, $Z_{i,k}$ and $Z_{j,k}$ are variable k for objects i and j respectively, and m is the number of variables (Gibrilla et al., 2011; Singh et al., 2004).

Principal component analysis (PCA)

PCA is a very effective tool used to reduce the dimension of a data set consisting of a large number of inter-related variables by reducing the contribution of variables with minor significance, while retaining as much variability of the data set as possible and

| Parameters | Abbreviation | Units | Methods |
|-------------------------|-------------------------------|-------------------------|-------------------------------------|
| Turbidity | Turb | NTU | Turbid metric method |
| Total solids 105°C | TS | mg/L | Gravimetric method |
| Total dissolved Solid | TDS | mg/L | Gravimetric method |
| Electrical Conductivity | EC | μS/cm | Calorimetric method |
| рН | рН | - | Calorimetric method |
| Ammonia | NH_3 | mg/l NH₃ | Aluminon method |
| Sodium | Na [⁺] | mg/l Na ⁺ | Flame photometer |
| Potassium | K^{+} | mg/l K ⁺ | Flame photometer |
| Total Hardness | TH | mg/I CaCO ₃ | Titrimetric method |
| Calcium | Ca ²⁺ | mg/l Ca ⁺² | Titrimetric method |
| Magnesium | Mg ²⁺ | mg/l Mg ⁺² | Periodate oxidation method |
| Total Iron | TFe | mg/l Fe ⁺³ | Phenanthroline Method |
| Fluoride | F ⁻ | mg/l F | SPADNS Method |
| Chloride | Cl | mg/l Cl ⁻ | Argentometric Method |
| Nitrate | NO_3^- | mg/l NO ₃ -2 | Cadmium reduction method |
| Alkalinity | Alkal | mg/I CaCO ₃ | Titrimetric method |
| Bicarbonate | HCO ₃ | mg/I HCO ₃ | Titrimetric method |
| Sulphate | SO ₄ ²⁻ | mg/I SO ₄ -2 | Turbid metric method |
| Phosphate | PO ₄ ³⁻ | mg/l PO ₄ 3- | Ascorbic acid, Molybdate blue metho |

Table 1. Water quality parameters, their units and methods of analysis.

interpreting the total variability of the dataset. This is accomplished by transforming the data set into a small number of new set of variables called Principal Components (PCs). The PCs are orthogonal (non-correlated), linear combinations of the originally observed water quality data and are arranged in decreasing order of importance (Shrestha and Kazama, 2007; Singh et al., 2004). The PCs can be expressed as:

$$Z_{ij} = a_{i1}x_{1j} + a_{i2}x_{2j} + a_{i3}x_{3j} + \dots + a_{im}x_{mj}$$
(2)

where Z is the component score, a is the component loading, x is the measured value of variable, i is the component number, j is the sample number and m is the total number of variables (Muangthong, 2015; Shrestha and Kazama, 2007).

Mann Kendall trend test

Mann-Kendall (MK) trend test is a rank-based and non-parametric statistical test used to detect trends and assess the significance of trends in hydro-meteorological time series data such as water quality, streamflow, temperature, and precipitation. This test is also documented to be more suitable and powerful for detecting trends of non-normally distributed and censored data (Yue et al., 2002; Xu et al., 2012) such as that of Awash River. It can be used in place of the parametric linear regression analysis, which requires that the residuals from the fitted regression line be normally distributed. Basically, it separately calculates the test statistics and variance of water quality data in each season after which overall statistics is calculated (Xu et al., 2012).

Assessment and validation of data errors and anomalies

Assessment of integrity and validity of a given dataset based on

knowledge, experience and intuition is an important and initial step of any water quality data analysis to draw meaningful conclusions from a study (Rangeti et al., 2015). It could be realized that the water quality dataset of Awash River basin has lots of errors and anomalies that need to be validated. The anomalies observed in the dataset were outliers, missing values and censored data. Among the observational (box-plots, time series, histogram, ranked data plots and normal probability plots) and statistical (Grubbs, Dixon, Cochran's C test and Mendel's h and k statistics) techniques available to test outliers, Dixon test was preferred since the number of values to be tested was greater than 6 and less than 25 and since the test was intended to be undertaken on non-normal raw data (Rangeti et al., 2015). It is based on the ratio of the distance between the potential outlier value and its nearest value ($Q_{\rm gap}$) to the range of the whole data set ($Q_{\rm range}$), as shown in Equation 4.

$$Q_{exp} = \frac{Q_{gap}}{Q_{rangs}}$$
(3)

If Q_{gap} is large enough as compared to Q_{range} , then the value is considered as an outlier. Dixon test was run excluding first only lake Beseka and then both lake Beseka and after Beseka sites on the same dataset. This resulted in outliers of parameters including alkalinity, HCO_3 , and SO_4^{2} at Meteka; TDS at office area and PO_4^{3} at Awash water supply since the two-tailed p-value (< 0.0001) was less than the significance level α =0.05. Running the test on each of the outlying parameters for the corresponding sites twice, the specific year and month, the effect was identified and appropraite correction was made. Therefore, some parameters values of specific months were not used to calculate the mean of the 9-years.

The outliers have come from technical and personal errors as the wrong calculation of average of the months' values, the wrong recording of the values like imperfect data entry while recording and transferring data, incorrect measurements due to equipment error,

Table 2. Mean values of water quality parameters for the ten sampling sites of Awash River basin during 2005-2013.

| par\site | Stat. | Dupti | Adaitu | Meteka | Off. Area | Weir Site | AwWSupp | Af. Bes | L. Bes | Bef. Bes | Wonji |
|-------------------|-------|---------|---------|---------|-----------|-----------|---------|---------|---------|----------|--------|
| Turb | mean | 1003.89 | 1435.71 | 674.36 | 1537.61 | 871.43 | 1650.40 | 1199.75 | 40.80 | 795.05 | 233.09 |
| Tuib | SD | 1283.52 | 538.44 | 477.99 | 951.35 | 561.38 | 1257.08 | 715.72 | 20.44 | 464.34 | 69.02 |
| TS | mean | 1914.78 | 3551.92 | 2369.96 | 3116.61 | 2255.12 | 3438.40 | 2453.73 | 4273.50 | 2040.39 | 490.02 |
| .0 | SD | 1641.66 | 1449.15 | 1338.07 | 1806.37 | 1122.53 | 1328.32 | 1420.73 | 613.61 | 1462.16 | 121.72 |
| EC | mean | 603.48 | 656.16 | 880.93 | 647.80 | 436.28 | 473.26 | 1164.12 | 5825.31 | 432.66 | 322.10 |
| | SD | 57.32 | 130.39 | 231.62 | 214.52 | 103.69 | 192.25 | 1062.65 | 606.16 | 202.72 | 35.42 |
| рΗ | mean | 7.98 | 8.32 | 8.23 | 7.88 | 7.90 | 7.90 | 8.03 | 9.42 | 7.72 | 8.25 |
| | SD | 0.17 | 0.61 | 0.61 | 0.19 | 0.23 | 0.27 | 0.46 | 0.17 | 0.38 | 0.87 |
| NH ₃ | mean | 0.51 | 0.88 | 0.48 | 0.76 | 0.67 | 0.75 | 0.94 | 0.66 | 0.73 | 0.65 |
| , | SD | 0.23 | 0.82 | 0.17 | 0.41 | 0.24 | 0.26 | 0.59 | 0.29 | 0.24 | 0.33 |
| Na⁺ | mean | 90.72 | 101.66 | 154.75 | 108.34 | 65.14 | 75.24 | 279.27 | 1474.85 | 63.73 | 36.09 |
| | SD | 13.36 | 25.51 | 51.76 | 53.49 | 28.98 | 52.90 | 311.44 | 190.30 | 58.71 | 8.53 |
| K [†] | mean | 6.06 | 7.35 | 11.11 | 9.70 | 9.56 | 9.04 | 11.77 | 55.55 | 10.31 | 6.93 |
| • | SD | 0.67 | 1.37 | 2.96 | 3.74 | 4.20 | 2.78 | 4.07 | 8.39 | 4.27 | 0.70 |
| Ca ²⁺ | mean | 35.83 | 32.65 | 31.87 | 33.42 | 31.19 | 29.06 | 26.71 | 6.25 | 31.22 | 28.55 |
| | SD | 6.69 | 4.07 | 1.89 | 4.74 | 1.82 | 4.02 | 6.37 | 1.82 | 1.60 | 1.12 |
| Mg ²⁺ | mean | 8.35 | 7.08 | 9.68 | 7.67 | 6.51 | 6.56 | 6.77 | 2.25 | 6.25 | 5.37 |
| 9 | SD | 2.64 | 1.03 | 2.32 | 4.24 | 2.07 | 3.61 | 4.57 | 1.62 | 2.86 | 1.33 |
| ГГе | mean | 0.34 | 0.20 | 0.14 | 0.37 | 0.23 | 0.25 | 0.27 | 0.15 | 0.27 | 0.25 |
| | SD | 0.76 | 0.16 | 0.06 | 0.34 | 0.16 | 0.20 | 0.16 | 0.08 | 0.21 | 0.17 |
| F ⁻ | mean | 1.39 | 1.45 | 2.12 | 2.07 | 2.01 | 1.43 | 5.65 | 25.43 | 1.67 | 1.49 |
| | SD | 0.39 | 0.49 | 0.31 | 0.27 | 1.08 | 0.49 | 6.27 | 9.64 | 0.60 | 0.38 |
| CI | mean | 42.37 | 47.73 | 61.51 | 44.25 | 25.91 | 27.64 | 91.11 | 492.06 | 24.16 | 15.57 |
| J . | SD | 8.64 | 12.16 | 19.24 | 20.19 | 10.50 | 16.65 | 93.80 | 68.65 | 17.45 | 2.79 |
| NO ₃ - | mean | 4.96 | 3.01 | 2.09 | 2.88 | 3.56 | 4.27 | 3.51 | 2.57 | 2.90 | 3.52 |
| 103 | SD | 7.33 | 1.47 | 0.86 | 1.08 | 1.16 | 2.76 | 0.77 | 2.35 | 1.02 | 1.61 |
| Alkal | mean | 196.88 | 224.93 | 320.05 | 242.95 | 182.22 | 187.08 | 439.54 | 2253.48 | 183.53 | 135.47 |
| ninai | SD | 25.70 | 35.84 | 79.76 | 72.33 | 46.90 | 75.58 | 372.52 | 396.43 | 86.70 | 18.14 |
| SO ₄ - | mean | 55.21 | 49.65 | 57.04 | 41.79 | 28.50 | 32.27 | 94.78 | 497.84 | 21.99 | 12.72 |
| 554 | SD | 13.61 | 13.10 | 24.05 | 22.73 | 16.15 | 21.17 | 101.47 | 116.34 | 16.97 | 6.34 |
| PO₄ ⁻ | mean | 0.45 | 0.80 | 0.62 | 0.79 | 0.48 | 0.54 | 0.86 | 2.68 | 0.46 | 0.50 |
| 1 04 | SD | 0.18 | 0.50 | 0.22 | 1.11 | 0.13 | 0.16 | 0.51 | 0.37 | 0.17 | 0.28 |

SD: Standard deviation; Stat.: statistic; Off. Area: office area; AwWSupp: Awash water supply; Af. Bes: after Beseka; L. Bes: lake Beseka, Bef. Bes: before Beseka. Concentration units are in mg/L except turbidity (NTU), EC (μ S/cm), and pH which is dimensionless.

Table 3. Eigenvalues.

| | F1 | F2 | F3 | F4 | F5 | F6 | F7 | F8 | F9 |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| Eigenvalue | 9.02 | 2.61 | 1.62 | 1.05 | 0.78 | 0.42 | 0.34 | 0.12 | 0.04 |
| Variability (%) | 56.39 | 16.32 | 10.10 | 6.57 | 4.87 | 2.62 | 2.13 | 0.75 | 0.26 |
| Cumulative % | 56.39 | 72.71 | 82.81 | 89.38 | 94.24 | 96.86 | 98.99 | 99.74 | 100.00 |

loss of sample before analysis or else. In the raw water quality dataset, there were a number of parameters of missing values and some censored data such as 'nil' and 'trace'. However, they were ignored while calculating the mean. Finally, all these errors were corrected with an informed decision and hence the 9-year mean could be changed.

Testing normality of the data, except turbidity, TS, NH₃, TFe, pH and Mg, all other parameters were not normally distributed since the significant values of both Kolmogorov-Smirnov and Shapiro-Wilk tests were relatively large (>0.05) for the normal ones but close to zero for the rest. However, transformation into normality, according to Singh et al. (2004), increases the influence of variables whose variance is small, reduces the influence of those whose variance is large and also eliminates the influence of different units of measurement thereby making the data dimensionless. Therefore, the variables were transformed to normal by Box-Cox (Osborne, 2010) variable transformation using SPSS and XLSTAT. After transforming, their normality was checked and proved to conform to normality.

Before analysis, suitability of the data for PCA was checked in terms of sampling adequacy and internal consistency of the data using Kaiser-Meyer-Olkin (KMO) and Cronbach's alpha, respectively. They are measures of testing consistency of variable values by offering information on whether or not data could be modelled with PCA. If the KMO value is greater than 0.50, it can be said that a dataset can be factorized (Sen et al., 2016; Ghosh and Jintanapakanont, 2004). Accordingly, for this study KMO was found to be 0.563 (>0.5). Additionally, it resulted in an overall Cronbach's alpha test score of 0.78 verifying internal consistency of the data. Both values imply that the sample was adequate and the desired multivariate statistical analyses (PCA) could suitably be applied on the dataset.

RESULTS

Principal component analysis (PCA)

Removing the three redundant variables TDS, TH and HCO₃⁻ from the list, which were highly correlated with others, PCA on the normalized 16 variables was then computed to produce significant PCs and to further reduce the contribution of variables with minor significance. It was done using Pearson type of correlation automatically without fixing the number of components/factors to be generated because of the width of the study area.

The 16 variables were reduced by PCA to 9 factors of which the first four showed Eigen values greater than unity. These were retained as the principal (significant) components (Shrestha and Kazama, 2007), because they could explain about 89.4% of the total variation

shown in Table 3. The table shows the sorted Eigen values (from large to small) and percentage of variability versus principal components.

A biplot of the variables and the sampling sites is shown by factors F1 against F2 in Figure 2. Both the plot and Table 4 indicate that F1 had a high and positive loading in TS, EC, pH, Na, K, F $^-$, CI $^-$, SO $_4^{2^-}$ and PO $_4^{3^-}$, which respectively were 0.69, 0.88, 0.79, 0.92, 0.85, 0.85, 0.89, 0.87 and 0.71. These large and positive loadings show strong linear correlation between the factors and parameters.

Cluster analysis

All the 10 sites of the basin are grouped by AHC into four statistically significant clusters at $(D_{link}/D_{max})\times100<20$. Results of application of the cluster analysis are best visualized by a dendrogram or binary tree as shown in Figure 3.

The dendrogram in Figure 3 clearly depicts grouping of the sites based on similarity of water quality characteristics. Accordingly, before Beseka, Weir site, Wonji and Dubti were grouped as cluster 1, while Adaitu, Office area, Awash water supply and after Beseka were grouped as cluster 2. However, Meteka and Lake Beseka are categorized as clusters 3 and 4, respectively.

Temporal trend analysis

Trend analysis of TDS, EC, pH, NH₃, Na, K, TH, F⁻, Cl⁻, and NO₃⁻ was performed in the 9 years period (2005 to 2013) by MK two tailed trend test for the 4 sites in the basin including Dubti, Office area, after Beseka and Wonji.

The analysis at 5% significant level in the dry season (December-February) of Dubti showed that except TH and F̄, none of the parameters were found to show any trend since their p values computed by exact method are greater than the significance level α =0.05. The test for the site revealed that TH had significant increasing and F̄ decreasing trend since their respective computed p-values, 0.011 and 0.03, were less than the significant level α =0.05 (Figure 4a). Similarly, the analysis of the office area indicated that only TDS showed a trend, which is monotonic upward throughout the years of

Table 4. Factor loadings, correlations and % contribution of the variables to the PCs (a) and % contribution of observations to the PCs (b).

| a) Loa | a) Loadings, Correlations and % Contribution of the Variables to PCs | | | | | | | | | | |
|------------------|--|-------|-------|-------|-------|--|------------|-------|-------|-------|-------|
| | | F1 | F2 | F3 | F4 | | | F1 | F2 | F3 | F4 |
| Turb | Load&Corr | -0.29 | 0.88 | 0.21 | -0.21 | Cl | Load&Corr | 0.91 | 0.32 | -0.19 | 0.16 |
| Tuib | % Contrib. | 0.92 | 29.71 | 2.69 | 4.16 | Oi | % Contrib. | 9.21 | 3.84 | 2.24 | 2.36 |
| TS | Load&Corr | 0.73 | 0.41 | 0.15 | -0.05 | NO ₃ | Load&Corr | -0.54 | 0.25 | 0.36 | 0.66 |
| 13 | % Contrib. | 5.84 | 6.33 | 1.35 | 0.20 | 1103 | % Contrib. | 3.25 | 2.37 | 8.07 | 40.97 |
| EC | Load&Corr | 0.92 | 0.29 | -0.19 | 0.13 | Alkal | Load&Corr | 0.97 | 0.19 | -0.12 | 0.05 |
| EC | % Contrib. | 9.45 | 3.21 | 2.32 | 1.63 | Alkai | % Contrib. | 10.32 | 1.33 | 0.95 | 0.22 |
| -11 | Load&Corr | 0.79 | -0.42 | -0.01 | 0.26 | SO ₄ ²⁻ | Load&Corr | 0.89 | 0.34 | -0.16 | 0.26 |
| pН | % Contrib. | 6.85 | 6.83 | 0.00 | 6.30 | SO ₄ | % Contrib. | 8.69 | 4.32 | 1.66 | 6.40 |
| . | Load&Corr | 0.15 | 0.40 | 0.79 | -0.31 | PO ₄ ³⁻ | Load&Corr | 0.88 | 0.16 | 0.19 | -0.14 |
| NH_3 | % Contrib. | 0.24 | 6.20 | 38.23 | 9.41 | | % Contrib. | 8.61 | 0.95 | 2.25 | 1.83 |
| | Load&Corr | 0.93 | 0.31 | -0.14 | 0.11 | 1 b) % Contribution of the Observations to PCs | | | | | |
| Na⁺ | % Contrib. | 9.53 | 3.70 | 1.27 | 1.08 | | | F1 | F2 | F3 | F4 |
| | Load&Corr | 0.84 | -0.18 | 0.11 | -0.29 | Dupti | | 7.73 | 6.31 | 13.74 | 59.21 |
| K ⁺ | % Contrib. | 7.78 | 1.28 | 0.76 | 7.95 | Adaitu | | 0.05 | 6.91 | 1.12 | 5.24 |
| o 2+ | Load&Corr | -0.72 | 0.50 | -0.42 | -0.01 | Meteka | 1 | 1.95 | 0.81 | 62.16 | 15.61 |
| Ca ²⁺ | % Contrib. | 5.69 | 9.67 | 10.89 | 0.01 | Off.Are | a | 0.02 | 16.16 | 0.48 | 2.68 |
| n a 2+ | Load&Corr | -0.48 | 0.54 | -0.61 | -0.25 | W.Site | | 2.50 | 2.03 | 0.15 | 0.37 |
| Mg ²⁺ | % Contrib. | 2.52 | 11.12 | 22.93 | 6.14 | Aw.W.S | Supp. | 2.08 | 3.01 | 8.70 | 0.01 |
| T F. | Load&Corr | -0.52 | 0.48 | 0.25 | 0.34 | Af.Bes. | | 6.51 | 8.88 | 8.61 | 0.12 |
| TFe | % Contrib. | 3.03 | 8.86 | 3.98 | 11.00 | | | 59.52 | 12.78 | 0.83 | 9.78 |
| | Load&Corr | 0.85 | -0.09 | 0.08 | -0.06 | Bef.Bes | S. | 3.93 | 2.61 | 0.54 | 6.72 |
| F ⁻ | % Contrib. | 8.08 | 0.29 | 0.41 | 0.35 | Wonji | | 15.71 | 40.51 | 3.68 | 0.27 |

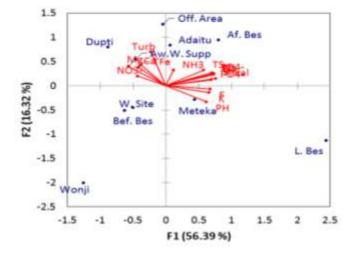


Figure 2. Biplot of sample sites and water quality variables (axes F1 and F2: 72.71%) obtained from principal component analysis.

consideration, and EC, NH₃, Cl⁻, Na and K also showed increasing trends only after 2009 (Figure 4b), but the rest were all found to show no trend at all. At Wonji in the dry season, except TH, none of the parameters indicated a trend from 2006 to 2013; TH has shown a significant increasing trend in the period (Figure 4d). The test is undertaken in the wet season (June-August) of the parameters and most of them were found to show no trend. However, TH and K, respectively at Dubti and Wonji showed a decreasing and increasing trends as depicted in Figure 4c.

Temporal trend analyses of the annual average values of turbidity, TS, TDS, EC, pH, NH₃, Na, K, TH, Ca, Mg, TFe, F, Cl, NO₃, alkalinity, HCO₃, SO₄²⁻ and PO₄³⁻ were undertaken throughout the nine years period by MK two tailed trend test for Dubti, Adaitu, office area, Weir site, after Beseka, Beseka, before Beseka, and Wonji. The analysis at 5% significant level for Dubti indicated that only SO₄²⁻ and F have shown increasing and decreasing

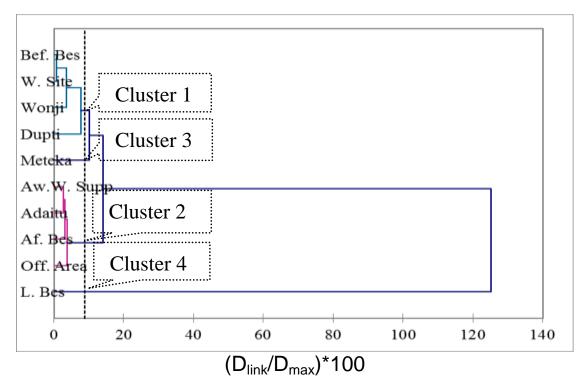


Figure 3. Dendrogram showing cluster analysis of sampling sites based on water quality characteristics of Awash River.

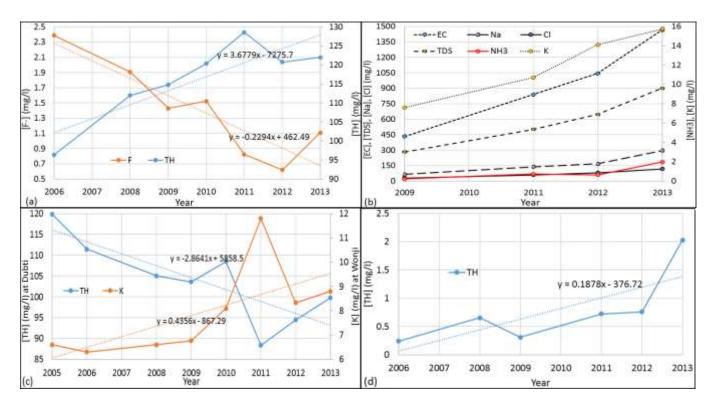


Figure 4. Temporal variation of TH and F⁻ at Dubti (a); EC, TDS, NH₃, Na, K, and Cl⁻ at the Office area (b); TH at Wonji (d) in the dry seasons and that of TH at Dubti and K at Wonji in the wet seasons (c).

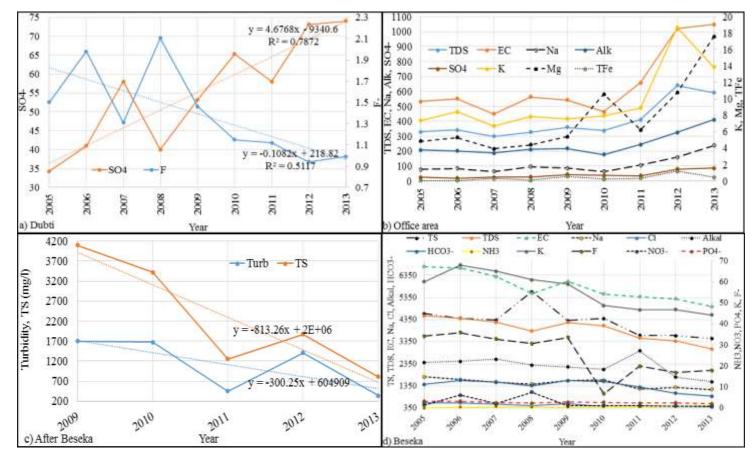


Figure 5. Trend analysis of the water quality data in the nine years' period at Dubti, Office area, After Beseka, and Beseka.

trends, respectively (Figure 5a), while all others did not as their p-values, computed by the exact and approximation methods, were greater than 0.05. A similar analysis at the office area indicated that TDS, EC, Na, K, Mg, TFe, alkalinity and ${\rm SO_4}^{2^-}$ showed an increasing trend since their computed p-value was lower than the significance level.

The test at Beseka revealed that TS, TDS, EC, NH₃, Na, K, F⁻, Cl⁻, NO₃⁻, alkalinity, HCO₃⁻ and PO₄³⁻ have shown trends since their p-values were smaller than alpha=0.05. At Beseka, all except NH₃ were decreasing. While both turbidity and TS showed a decreasing trend at Beseka, the rest were found to show no trend at all. On the other hand, performing MK test on NH₃, K, Mg, TH and SO₄² showed an increasing trend, while F⁻ showed a decreasing trend at Wonji as their p-values is lower than the significance level alpha=0.05, others did not show at all.

Before Beseka, TDS, EC, NH₃, Na, K, TH, TFe, CI, alkalinity, and HCO₃ showed a trend from 2005 to 2013, while at Weir site, TDS, EC, NH₃, Na, K, Mg, TFe, CI, alkalinity, HCO₃, SO₄², and PO₄³ showed a trend. With a similar argument MK test indicated at Adaitu that only

EC, NH₃, HCO₃, and SO₄² showed trends (Figure 5).

Spatial trend analysis

Spatial analysis of water quality parameters was assessed at the 14 sampling sites of Awash River Basin. From slopes of trendlines of graphs of the water quality indicators, it can be seen that as one moves from the upper to lower parts of basin in the dry season (October-January), EC, TH and Cl⁻ levels were observed to be decreasing (Figure 6). From the trendlines of the graphs, one can also observe that TH was slightly increasing while TDS, Cl , and ${\rm SO_4}^{2^-}$ were decreasing in the same direction in the rainy season (June-September). It can also be seen from the graph that among the sites in both dry and wet seasons, CI and EC/TDS/SO₄²⁻ were maximized, respectively, at Beseka and before Beseka. At Beseka in both seasons, TH showed a trend opposite to that of EC/TDS/SO₄², that is, it revealed an absolute minimum. The most important sites responsible for the spatial variation were Beseka, before Beseka and Sodere spring since it was there, where for instance, EC, TDS,

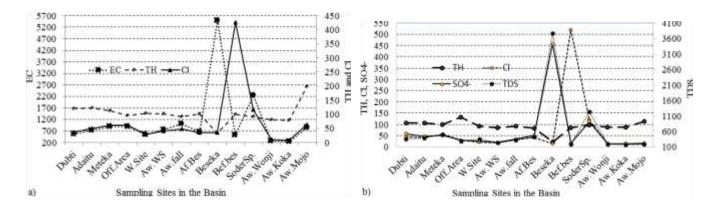


Figure 6. Spatial variation of EC, TH, and CI in the dry (a) and TH, CI, SO42- and TDS in the wet (b) seasons of Awash River basin.

TH, Cl, and SO₄²⁻ showed significant variations.

DISCUSSION

As shown in Table 4, the analysis of PCA revealed that the first component, explaining about 56.39% of the variance, was strongly and positively correlated with TS, EC, pH, Na, K, F⁻, Cl⁻, alkalinity, $SO_4^{2^-}$ and $PO_4^{3^-}$ and negatively to Ca and TFe. The second component of 16.32% variability explanatory had a relatively high and positive loading on turbidity, calcium and magnesium. The third and the fourth ones were positively related respectively to NH₃ and NO₃. From the table of correlation (percentage contributions) of variables to the four principal components, it could be observed that F1 is affected mostly by TS, EC, pH, Na, K, F⁻, Cl⁻, alkalinity, $SO_4^{2^-}$ and $PO_4^{3^-}$; F2 by turbidity, Ca and Mg; F3 by NH₃ and F4 by NO₃.

When contribution of each of the sites to the factors is examined with reference to Table 4, the largest percentage of about 59.5 for F1 was taken by Lake Beseka. This is consistent with the respective factor loading values (0.69, 0.88, 0.79, 0.92, 0.85, 0.85, 0.89, 0.87 and 0.71) of TS, EC, pH, F⁻, Cl⁻, Na, K, SO₄²⁻ and PO₄³⁻ of the water being taken from the sites. Similarly, it can also be seen from Table 4 that among the remaining sampling sites F2 was affected mostly by Wonji, F3 by Meteka, and F4 by Dubti and hence these sites are considered as the most important pollution generators. However, the pH values of the 10 stations in Table 2 showed generally less variation with the range being only from 7.72 to 9.42.

Grouping of the before Beseka, Weir site, Wonji and Dubti into cluster 1 seems to be reasonable as these sites look like that they all are in the vicinity of specialized sugarcane state farms. The fact that Adaitu, office area, Awash water supply and after Beseka are grouped as

cluster 2 is consistent with the ground truth that the sites receive waste contributing to turbidity, TS and NH₃ from the dominantly urban and bare-lands. Meteka seems to be unique in that it receives waste from small subsistence-oriented and diversified agricultural and rural areas. Similarly, Lake Beseka is unique in that the lake water quality is by far different from others as it shows the highest values of almost all parameters except for turbidity, TH, Ca, Mg, TFe and NO₃. This is confirmed by the study of Dinka (2016) who has urged in his conclusion to avoid even the contact of Lake Basaka water to crops and productive soil in the region because of its pollution.

The MK test at Beseka resulted in the fact that TS, TDS, EC, Na, K, F', Cl', NO₃, alkalinity, HCO₃ and PO₄ showed decreasing trends. This finding is in agreement with that of Dinka (2017) who found that in the previous two decades (1960-1980) water quality parameters especially ionic concentrations had shown decreasing trends in response to the fast increasing volume of the lake, which has a dilution effect although his finding has unexpectedly shown stability of most and even increasing trend of other parameters post 2000. Throughout the years from 2005 to 2013, almost all parameters except NH₃ in Figure 5d were showing a temporal decreasing trend. This is suggested to be due to ever increasing volume of the lake from time to time which could dilute the water more (Alemayehu et al., 2006; Dinka, 2017).

On the other hand, EC (salinity-determinant) has shown a spatially increasing trend from upper to middle and then decreasing afterwards (Figure 6), though it was concluded by Taddese et al. (2003) that salinity is generally increasing from the upper to lower basin. The state of EC being maximum in the middle seems, however, to be reasonable since there are Lake Beseka and Sodere spring here having high EC values. Cl has also shown a similar trend as EC throughout the basin while TH showed decreasing trend in the upper and

| LUCIacasa | 20 | 00 | 2014 | | | |
|--------------------|-----------|---------|-----------|---------|--|--|
| LU Classses | Area (ha) | Percent | Area (ha) | Percent | | |
| Agriculture | 2419874 | 21.3% | 3233580 | 28.1% | | |
| Forest | 1567171 | 13.6% | 1290576 | 11.2% | | |
| Grassland | 1599050 | 13.9% | 1390025 | 12.1% | | |
| Shrubland | 1546467 | 13.4% | 1590415 | 13.8% | | |
| Barrenland | 3052142 | 26.5% | 2631510 | 22.8% | | |
| Sandy/Exposed rock | 944903 | 8.2% | 754349 | 6.5% | | |
| Builtup area | 261478 | 2.3% | 541663 | 4.7% | | |
| Waterbodies | 102724 | 0.9% | 85190 | 0.7% | | |

Table 5. Percentages of land uses of the basin in 2000 and 2014.

increasing trend in the middle and lower sub-basins. Most other pollutants (discharged into the River from the upper basin) are also seen to decrease their concentraion in the downstream (except for EC, TDS, SO₄, and Cl at lake Beseka and Sodere hot spring). This might be due to the natural purification process taking place in the course of the river and the lesser amount of waste discharged into the river in the middle and lower basins though the climate is worsening in the downstream tending to concentrate the pollutants while concurrently diminishing the volume of the river due to diversion for different purposes in the lower part.

Comparison of water quality with the land uses in the basin

The 2000 and 2014 SRTM images of the basin have been layer stacked, mosaicked and classified by maximum likelihood supervised classification of technique. Then area in hectare (ha) and percentage statistics for the classified images of each land use class in the two years around which the water quality data were collected have been computed. Table 5 clearly shows why some parameters like SO₄, TH, EC, Na, Cl, K, and NH₃ increase monotonically at some sites and why the rest vary in the other sites of the basin temporally, which is corresponding to the land use changes in the respective sites. For instance, agriculture and built-up areas have significantly increased in the basin from 2000 to 2014. The associated pollution by agro-chemicals, nutrients, and hardness resulting from urbanization and agricultural intensification was observed.

From the 2014 land use map (Figure 1), the land is more degradable as one moves from upper to lower basin. The land in the lower part of the basin is mostly bare, sandy, rocky and the rest is covered by shrubs, which is an indication of an arid zone. In the middle part of the basin, there are Lake Beseka and Sodere hot spring, both of which are located in a tectonically active

Main Ethiopian Rift region and discharge to Awash River. Lake Beseka is not only the fastest growing unlike other lakes in the region but also unique in its water quality characteristics (Dinka, 2017; Alemayehu et al., 2006). The exceptional pollution of this lake and at the site just before it was found in this study by parameters as EC, TDS, SO₄ and Cl, is in line with these findings. This is found to be due to the underlying anthropogenic (increased discharge of the hot springs and discharge of huge amount of irrigation wastewater upstream of the lake, discharges from factory and domestic sewage), natural (weathering of rocks, soil erosion, sediment loading, deposition of animal and plant debris, and solution of minerals in the basin), climatic and geologic factors (Goerner et al., 2009; Dinka, 2017).

Conclusion

Spatial-temporal water-quality analyses usually involve huge multi-dimensional data that need multivariate statistical methods. The PCA resulted in four principal components representing the whole dataset and most parameters are shown by the analysis to vary spatially. It could also identify the most contributing sites and parameters for the principal components. The most sensitive site for the variation is found to be Lake Beseka for which appropriate management need to be sought. Here, agglomerative hierarchical cluster analysis is used to group the ten sampling sites into four clusters pertaining to water quality characteristics. The seasonal MK trend test detected that most of the parameters show temporal as well as spatial trends. If special attention is not payed to the water quality parameters that show a monotonic increasing trends such as EC, TDS, Na, alkalinity, SO₄², NH₃, K, and Cl at the Office area; K, Mg, SO₄² at Wonji; and TH in all the sites, the water quality of the river in particular and the basin in general will deteriorate to the extent that it will not be fit for any intended uses. Thus, the multivariate statistical techniques

were proven to be excellent exploratory tools in the analysis and interpretation of the complex dataset on water quality and in understanding their temporal and spatial variations.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Full Length Research Paper

Two-stage anaerobic sequence batch digestion of composite tannery wastewater

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Most of the leather industries in Ethiopia discharge their effluent partially or without any treatment to the nearby water bodies. This creates a serious effect on aquatic biota and surrounding environment due to its high organic loading and chromium content. To minimize the effect, tannery wastewater should be treated before the effluent is discharged to the environment. Therefore, the main objective of the study was to use a two stage laboratory scale Anaerobic Sequence Batch Digester (Reactor) in order to investigate the potential of composite tannery wastewater to produce biogas. Two Stage Anaerobic Sequence Batch Digester was used because it has a conducive environment for microorganisms at different temperature. The present study characterized composite tannery wastewater with respect to biogas production parameters. Four sets of conditions were investigated: Mesophilic to mesophilic; thermophilic to thermophilic; mesophilic to thermophilic and thermophilic to mesophilic in the hydrolysis/acidification and methanogenesis stages (reactors), respectively. The Organic Loading Rate (OLR) was ranged between 9.58 and 10.28 kg COD/m³ day throughout the study. The highest volume of biogas (7232 ml) and content of methane (69.75%) was in the thermophilic-thermophilic phase. The removal efficiency of total solid (TS) and volatile solids (VS) of all digesters were in the range of 52 to 69 and 58 to 81%, respectively, treatment of composite tannery wastewater by a two stage Anaerobic Sequence Batch Digester (Reactor) (ASBR) produces high amount of methane at thermophilic - thermophilic phase and the lowest produced in mesophlic mesophlic phase. Digesters in mesophilic-thermophilic (D₃) produced higher biogas and biogas quality than digesters with thermophilic- mesophlic (D₄) ones.

Key words: Anaerobic sequential batch reactor, wastewater to energy, tannery wastewater management.

INTRODUCTION

With a rapidly expanding human population and a growing trend of industrial development added with

limited technological advancement, problems related to the management of industrial waste have become a

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major problem in Ethiopia (Leta et al., 2004).

In Ethiopia, there are more than 20 tanneries (EPA, 2003). Accumulation of large volumes of dried-sludge in treatment compound has become common (Leta et al., 2004). This has immediate public health implications, which are manifested as frequent outbreak of major epidemic diseases and also contributes to climate change as it releases greenhouse gases; methane and carbon dioxide (Abera, 2010).

The industrial strategic development plan of Ethiopia gives great emphasis to improve export-led products to join the international market in large-scale such as leather products. Emphasis has been given to ensure faster and sustained development of the industry sector in Ethiopia in the next five years of the Growth and Transformation Plan.

Industry zone development as the potentially suitable towns and cities of the country has been found as an irreplaceable measure to create favorable conditions for implementing industry development in the country. However, in Ethiopia most of the leather industries discharge their effluent without any treatment to nearby rivers (EPA, 2003; Leta et al., 2004). This creates a serious effect on aquatic biota and the surrounding environment.

The main objective of this study was to investigate the potential of composite tannery wastewater to produce biogas using a two stage laboratory scale Anaerobic Sequence Batch Digester (Reactor) (ASBR). Two stage ASBR was used because it has a conducive environment for micro-organisms at different temperature, and it reduces the effect of shock loadings to the methanogenic reactor, and increases the stability of the two phase system.

MATERIALS AND METHODS

Sample collection and preparation

Tannery wastewater samples were collected from Modjo Tannery, central Ethiopia using different size plastic bags every seven days for three months. The samples were collected from three different effluent lines which included the sulfur line; chrome line and general wastewater line. Five hundred cubic meter of wastewater is released from Mojo Tannery per day, from this, 160 m³ is from the sulfide line, 100 m³ is from chrome line and the rest 240 m³ is from general wastewater line in the ratio of 1.6:1:2.4, respectively. Using measuring cylinder based on the aformentioned ratio, the composite samples were prepared at Modjo Tannery, and for every seven days, 20 L composite sample was prepared and transported to the research lab at the Centre for Environmental Sciences, Addis Ababa University, and stored at 4°C in the refrigerator until it was added to the digester for treatment.

Experimental set up of the two-stage anaerobic sequential batch reactor (ASBR)

Two parallel anaerobic digestion systems consisting of four ASBRs

in series were tested. The temperatures in this study were controlled at mesophilic condition (35±2°C), and at thermophilic condition (55±2°C). The two reactors in the first system were operated at the same temperature, D1:35°C and 35°C (mesophilic) and D2: 55°C and 55°C (thermophilic), respectively. The two reactors in the second system were at two different temperatures D3: 35°C and 55°C (mesophilic to thermophilic) and D4: 55°C and 35°C (thermophilic to mesophilic), respectively. Each reactor had a total liquid volume of 2.8 L. Totally eight reactors were prepared to observe the potential of composite tannery wastewater for production of biogas. In this experiment, each treatment was run in triplicates. The system was adapted from Dugba and Zhang (1999).

To create the anaerobic condition, the bottles were covered by rubber stopper having two hoses at the top and sealed with a gas kit maker to make oxygen free environment inside the digester. The two hoses on the top of the bottles had different purposes. In the first stage (acidogenic), the first hose was stretched up to the bottom of the solution enabling decanting of all the solution to the second stage (methanogenesis). While the second hose was placed above the solution for transferring the produced gas to gas collector plastic bag.

In a similar manner, the second phase (methanogenesis) reactors had also two hoses at the top. The first hose was immersed up to half-height of the reactor and used for filling of the solution from the first stage and decanting the solution. While the second hose was above the solution, and it channeled the produced gas to the plastic bag, which was used to collect the produced biogas (Figure 1).

The objective of the acidogenic reactor was to acidify the composite tannery wastewater in an effort to improve the performance of the methanogenic reactors. The acidogenic reactor was fed the composite tannery wastewater from Mojo Tannery.

Operation of the ASBR

The study was conducted for 90 days (3 months) in two different operational phases. The first phase at the startup period of the ASBR was operated for 30 days from January 3/2013 to February 2/2013. This time was assigned for accumulation of biomass. During this period, the digester was operated in 24 h cycle mode, whereas 20 h was given for the reaction phase (T_R) and 3 h given for settling (T_S).

To have a good biomass settlement, the supernatant was manually decanted from the upper most of the reactor for 30 min with the help of pump drivers (PD 5206) at a speed of 606 rpm. Batch feeding was performed mechanically through the top of the reactor at the beginning of the next cycle for 30 min at the same speed as the substrate was decanted.

During the second phase, the ASBR was operated for 60 days (2 months) from February 3 to April 2, 2013, with a different cycle time from the first phase. The reactors were operated at a 48 h cycle mode, where 46 h was given for the reaction period (T_R), 1 h for settling (T_S) and the remaining 1 h was for filling and decanting, operated in the same way as in the first phase.

The organic loading rate (OLR) for the two-stage ASBR was adjusted to be steady. However, due to fluctuations in the composition of the raw wastewater, it was difficult to maintain a steady OLR, and the actual OLR was between 9.58 to 10.28 kg COD/m³-day throughout the study.

Chemical analysis

The characteristic of the composite tannery wastewater as feedstock for biogas production was carried out using its total solids



Figure 1. The two-stage ASBR setup.

Table 1. Characterization of composite wastewater in terms of biogas production parameters.

| Parameter | Composite tannery wastewater |
|----------------------|------------------------------|
| Moisture content (%) | 91.94 |
| TS (%) | 8.06 |
| VS(% based on TS) | 73.23 |
| Ash (% based on TS) | 26.77 |
| OC (%) | 40.68 |
| TN (%) | 1.53 |
| C/N ratio | 26.58 |
| рН | 9.49±1.15 |

(TS), volatile solids (VS), total nitrogen (TN) and carbon and nitrogen contents by APHA 20E 4500 NB (1999) instruction.

Biogas quantity and quality determination

The volume of biogas produced was measured when the supernatant was manually decanted and at the starting of the next cycle by directly measuring the volume of the gas collector bag. The sum of the total volume of the acidogenic and methanogenic reactors gave the total biogas produced by the system. Quality of biogas was measured by biogas analyzer weekly until the gas produced plateaued. The plastic bag which was filled by the biogas during measuring the volume was directly connected to the calibrated biogas analyzer, and the percentage of methane was displayed on the analyzer.

RESULTS AND DISCUSSION

Characterization of Modjo Tannery Composite wastewater in terms of biogas production parameters

The averaged values of TS, VS and C/N ratio of the feedstock are presented in Table 1. The average moisture content of the composite tannery wastewater was 91.94%. The average TS of the substrate was 8.06%, the appropriate amount of the feedstock as the most favorable percentage of TS for biogas production is in the range of 8 to 10% (Jurgen et al., 2009; Ituen et al., 2007). In general, the TS value for composite tannery wastewater in this study varied from 5.64 to 10.68%.

Out of the TS, VS and ash (fixed solids) content of the substrate were 73.23 and 26.77%, respectively. As VS is organic material that can be decomposed, it shows the potential for further digestion. This indicates that a large fraction of composite tannery wastewater is biodegradable, and thus it can serve as an important feedstock for biogas production (Table 1).

The average value of OC% and TN% in this study were 40.68 and 1.53, respectively. Methane yield and its production rates are highly influenced by the balance of carbon and nitrogen in the feeding material. The average C/N ratio in this experiment was 26.58, which is similar to the value 20:1 to 30:1 reported by Dahlman and Forst (2001). Pyle (1978) stated that optimum C/N ratio recommended for an anaerobic digester was 10 to 30. Generally, the balance of carbon and nitrogen of the

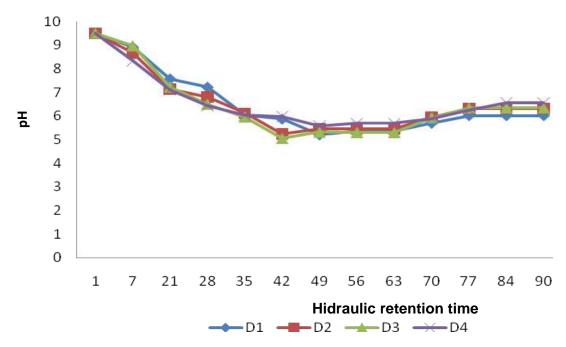


Figure 2. Average pH values in the acidogenic phase.

composite tannery wastewater was good to be used for anaerobic digestion to produce biogas.

Characteristics of digesters

pН

The pH of each digester was maintained between 6.02 to 7.66. The findings for both reactors are shown in Figures 2 and 3.

Acidogenic reactor

In the first week of the startup period, the pH of the substrate in the reactor was between 9.49 to 8.13, in the following weeks the pH decreased. This is due to the formation of acids by acidogenic bacteria during the incubation period. Figure 2 shows the average result of the pH in acidogenic reactor.

As seen Figures 1 and 2, the pH of all the digesters showed a sharp decline at the beginning of the digestion period and kept declining up to the 45th day of fermentation. The decrease in pH is a function of the concentration of volatile fatty acids produced by the activity of hydrolytic acidogenic bacteria capable of degrading the feedstock in the first few days of incubation, bicarbonate alkalinity of the system, and the amount of carbon dioxide produced (Gomec ans Speece 2003).

Nina et al. (2011) verified that the presence of fat can raise the formation of volatile fatty acids, leading to a fall in pH. The composite tannery wastewater from raw hide and skins processing at Modjo Tannery contains high amount of fat, therefore in this study there was no need of adding or adjusting substances like lime, ash or ammonia (pretreatment methods) as the gas producing bacteria was able to ferment the acid or alkali, and restore balance as reported by Saxon (1998).

Generally, the average value of the pH in the acidogenic reactor in this study was 6.02±0.51 almost similar to the value of 5.7 to 5.8 reported by Kasapgil et al.(1995) as best pH for the acid phase reactor. According to Antonopoulou et al. (2008), the optimum pH value for acid producing bacteria is from 5 to 6.

Methanogenic reactor

The methanogenic reactor was fed the acidified composite tannery wastewater from the acidogenic reactor. Figure 3 shows the average result of pH in the methanogenic reactor. As seen in Figure 3 after 21 days, the pH of the reactors increased which is an indication of the digestion of volatile acid and nitrogen compounds, and more methane being produced. The production of acids and its digestion continued up to 56 days of digestion, and the pH remained constant after the 56 days which is due to the presence of larger number of methanogenic bacteria in the reactor, and almost all the

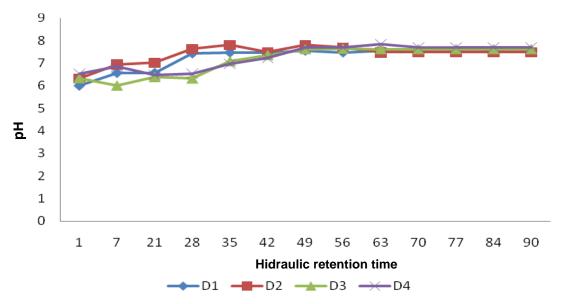


Figure 3. Average pH values in the methanogenic phase.

acidic wastewater fed from the Acidic Reactor present could be digested to form methane and carbon dioxide gases. The pH of the methanogenesis reactor in this study ranged from 6.30 to 7.66, and with an average pH of 7.26±0.3 over the duration of the study. pH range of 6 to 7 is very suitable for optimum biogas production due to the normal functioning of methanogenic bacteria in this pH range (Ozmen and Aslanzadeh, 2009). According to Antonopoulou et al. (2008), the optimum pH in the reactor should be in the range of 6.5 to 8, as this is suitable for acetogens and methanogens. Generally, this study revealed that it is possible to produce biogas from composite tannery wastewater at pH range of 6.02±0.51 in acidogenic phase and 7.26±0.3 in methanogenic phase.

Quantity and quality of biogas production

Biogas production and its methane content were measured for about thirteen weeks of digestion period until the gas production became stable. The quantity and quality of biogas production for the two phase system were estimated by adding the daily biogas produced from the acidogenic and methanogenic reactors. Although the acidogenic reactor produced a fair amount of biogas, the methane content was fairly low (less than 10%), and therefore contributed very little to the overall biogas methane content.

Quantity of biogas produced

It was found that D₂ (thermophilic-thermophilic) produced

the highest volume of biogas (365 mL) in the first week of the digestion. During this period, the other digesters produced below 200 mL as indicated in Figure 4.

The average daily biogas production (volume) in almost all digesters increased persistently up to the six week and for D_1 (mesophilic - mesophilic), the increment continued up to the eighth week. As the increase in temperature has a positive effect on biogas yield, most of the biogas was produced at thermophilic phase. Moreover, in the mesophilic range, the bacterial activity and growth decrease by one half for each 10°C drop below 35°C (Hulshoff, 1995). Thus, for a given degree of digestion to be attained, the lower the temperature, the longer is the digestion time.

There was a continual growth in biogas production with temperature increase as shown in Figure 4. Thus, the digesters in thermophilic temperature range produced more biogas and they reached their stable period within shorter time than the mesophlic ones. The highest values of the daily biogas production in each digester in their stable period were: 156, 699, 344 and 292 mL respectively from D_1 to D_4 . D_2 (thermophilic-thermophilic) produced highest amount of biogas and stable production within the six weeks, and D_1 (mesophilic – mesophilic) produced the lowest amount of biogas and reached stable period within eight weeks. The acetogenic and methanogenic stages act as continuous reactors, which results in constant gas production (Chaudhary, 2008).

The average chemical oxygen demand (COD) after anaerobic digestion of composite tannery wastewater was 5100, 3550, 3850 and 4650mg/l, respectively from D1 to D4. Considerable removal efficiencies for COD were achieved (57.42, 70.36, 67.86 and 61.18%, respectively), recorded from D1 to D4. The main reason

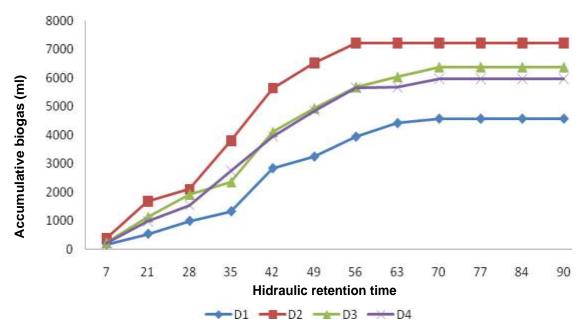


Figure 4. Comparison of the average daily biogas production.

for good removal of COD could be related to the presence of optimum environmental conditions such as temperature and pH required for anaerobic acetogenic and methanogenic bacteria. According to Metcalf and Eddy (1991), environmental factors that affect biological organic matter removal are pH and inhibitory substances.

The highest total biogas (7232 mL) was produced by D_2 , and D_1 produced the least biogas (4153 mL). Digesters D_3 and D_4 produced 6375 and 5975 mL, respectively. The results of this study indicates that the highest total biogas production was in thermophilic-thermophilic relationship than the mesophilic-mesophilic. It is well known that the anaerobic biodegradation is faster in thermophilic reactors (Gómez, 2011). Idnani and Varadarajan (1974) observed that there was less gas production below 30°C, and the optimum temperature for biogas production was 40 to 50°C.

Further, the results of this study indicate that the mesophlic to thermophilic digesters produced high biogas than the thermophilic to mesophlic reactors. This is due to stability of microorganisms and change in temperature. Bolzonella et al. (2005) reported that thermophilic microorganisms are less stable than mesophlic ones, and Anonymous (1992) indicated that a stable temperature is very important to maintain gas production as the bacteria are very sensitive to changes in temperature.

Quality of biogas produced

The acidogenic reactor produced more biogas than the

methanogenesis, of which the methane content was insignificant (less than 10%). Zhang et al. (2010) showed that during the two phase sludge anaerobic digestion, the sludge was hydrolyzed and acidified in the first phase, and then methane was produced in the second stage.

In connection to this, Ince (1998) and Kasapgil et al. (1995) reported methane percentages of 5 to 15 and 7 to 27 in acidogenic reactor. In this study D_2 in the acidogenic phase produced 22.4% of methane. This is due to high temperature (55°C) in the acidogenic phase. Due to the low methane content of the biogas from the acidogenic reactor and the high methane content in the biogas of the methanogenic reactor, it can be concluded that separation of the two phases was essential. Figure 5 shows the weekly biogas quality (Methane, CH_4) produced by each digester.

The quality of biogas produced by each reactor for four weeks of digestion period was below 50%. In this study, D_2 (thermophilic-thermophilic) reached stable production within six weeks whereas D_1 (mesophilic – mesophilic) reached its stable period within eight weeks. The growth rates of thermophilic methanogens are 2 to 3 times longer than those of mesophilic ones (Van Lier et al., 1993; Mladenovska and Ahring, 2000).

The percentage composition of methane was between 51 to 69 during the operational period. These values agree with the theoretical yield of 50 to 75% as suggested by Yadava and Hesse (1981). The highest cumulative biogas quality was produced by D_2 (69.75), and the lowest cumulative biogas quality was produced by D_1 (51.42). Digesters D_3 and D_4 produced cumulative

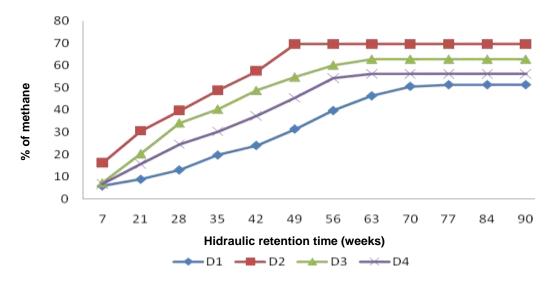


Figure 5. The weekly percentage of methane in biogas for each digester.

Table 2. The value of TS and VS after AD.

| Treatment | TS (%) | %VS | Removal efficiency of %TS | Removal efficiency of % VS |
|----------------|--------|-------|---------------------------|----------------------------|
| D ₁ | 3.79 | 30.56 | 52.97 | 58.27 |
| D_2 | 1.76 | 13.87 | 78.16 | 81.05 |
| D_3 | 2.47 | 18.32 | 69.35 | 74.98 |
| D_4 | 3.37 | 25.47 | 58.18 | 65.21 |

biogas quality were 62.86 and 56.18, respectively.

The thermophilic process is the most efficient in terms of organic matter removal and methane production (Zabranska et al., 2000; Ahring et al., 2003). The reason for this is that the growth rates of thermophilic methanogens are higher than those of mesophlic methanogens (Duan and Mao, 2006).

The results of this study shows the possibility of producing high quantity and quality biogas from composite tannery wastewater without addition of other co-digesters except starter (inoculants). The highest cumulative biogas 7232 mL and biogas quality 69.75% yield was recorded for the digester at thermophilic phase, which is represented by $D_{\rm 2}$ in this study.

Characteristics of the effluent

Physical properties of the effluent

The amounts of TS and VS that were retained in each of the digesters were measured. Table 2 shows the average values of percentages of TS and VS of the effluent of each digester.

About 52.97, 78.16, 69.35 and 58.18% reduction of TS was observed for digesters D₁ to D₄, respectively. High and low removal efficiency of TS (%) was seen for D₂ (thermophilic-thermophilic) and D_1 (mesophilic mesophilic). In mesophilic range, a considerable proportion of solid compounds are recalcitrant, which leads to poorer efficiencies in inorganic solids removal and methane production (Braber, 1995). As seen in Table 2, percent reduction in VS were 58.27, 81.05, 74.98 and 65.21, respectively for digesters D₁ D2, D3 Aand D₄. Similarly, high and low removal efficiency of VS was seen for D₂ (thermophilic-thermophilic) and D₁ (mesophlicmesophlic).

According to Tsegaye et al. (2016), the relative higher removal efficiency of VS (%) than the TS (%) was a very good indication of high uptake rate of the organic fraction of total solids and the effectiveness of the anaerobic reactor. The ratio of VS/TS before digestion was always relatively higher than the ratio after digestion, which is an indication of the utilization of the organic fraction during the anaerobic digestion. The VS/TS ratio in this study before digestion was 9.08 while after digestion 8.06, 7.88, 7.41 and 7.55 were observed for digesters D₁ to D₄, respectively.

Table 3. Average pH of the effluent.

| Digester | D ₁ | D_2 | D ₃ | D_4 |
|----------|----------------|-------|----------------|-------|
| pН | 7.18 | 7.59 | 7.61 | 7.67 |

pH of the effluent

The average pH value of the effluent for each digester is summarized in Table 3. The average pH value of the effluent varied from 7.18 to 7.67. The minimum and maximum pH accepted values for slurry was 6.0 and 8.5, respectively (Fokhrul, 2009). In addition, Williams (1998) reported the values lie in the range of the pH of the compost 6 to 7.

Conclusion

The current study demonstarted that composite tannery wastewater has a great potential for the production of biogas using two stage anaerobical sequential batch reactors under thermophilic conditions which create alternative source of renewable energy. Moreover, this system of managing wastewater significantly contributes towards resosurce-recovery and pollution managemnt around tannery industry.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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