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Table of Contents: Volume 11 Number 2 February 2017

ARTICLES

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Full Length Research Paper

Residents' perception of solid waste disposal practices in Sokoto, Northwest Nigeria

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Proper waste disposal is a key to protecting public health. Thus poorly managed and disposed waste encourages breeding of insect vectors and exposed public to increase risk of infection. This study aimed at determining the residents' perception about waste disposal in Sokoto metropolis. This was a descriptive cross-sectional survey conducted in Sokoto metropolis. A two stage sampling technique was used to select the survey participants. A set of interviewer-administered questionnaires were used to collect field data. Ethical clearance was obtained from state research ethics committee and in addition, individual informed consent was obtained before questionnaires were administered. Average age of the respondents was 30 years with 50% aged between 25 and 44 years. Large proportion (47.4%) of the respondents had only Quranic education. Majority (94.1%) of the respondents expressed worries about the indiscriminate littering of the metropolis with waste and more than half (55%) reported that residents were responsible for the state of poor sanitation while 38% felt it was fault of government. Although, 91% of respondents said it is appropriate for residents to clean own surroundings, 41% felt residents alone should take sole responsibility for the cleaning; while 40% felt government and residents should take joint responsibility. Less than half (46%) of respondents reported that improper waste disposal have health related problems. Although, majority respondents were disturbed with the way refuse litters the state metropolis, many are unaware of its health related problems. There is need to create awareness among general public of consequences of poor refuse disposal.

Key words: Perception, solid waste, disposal, Sokoto.

INTRODUCTION

Solid wastes are waste generated through domestic, commercial, industrial, agricultural and other social activities including institutional wastes, street sweepings and construction debris.

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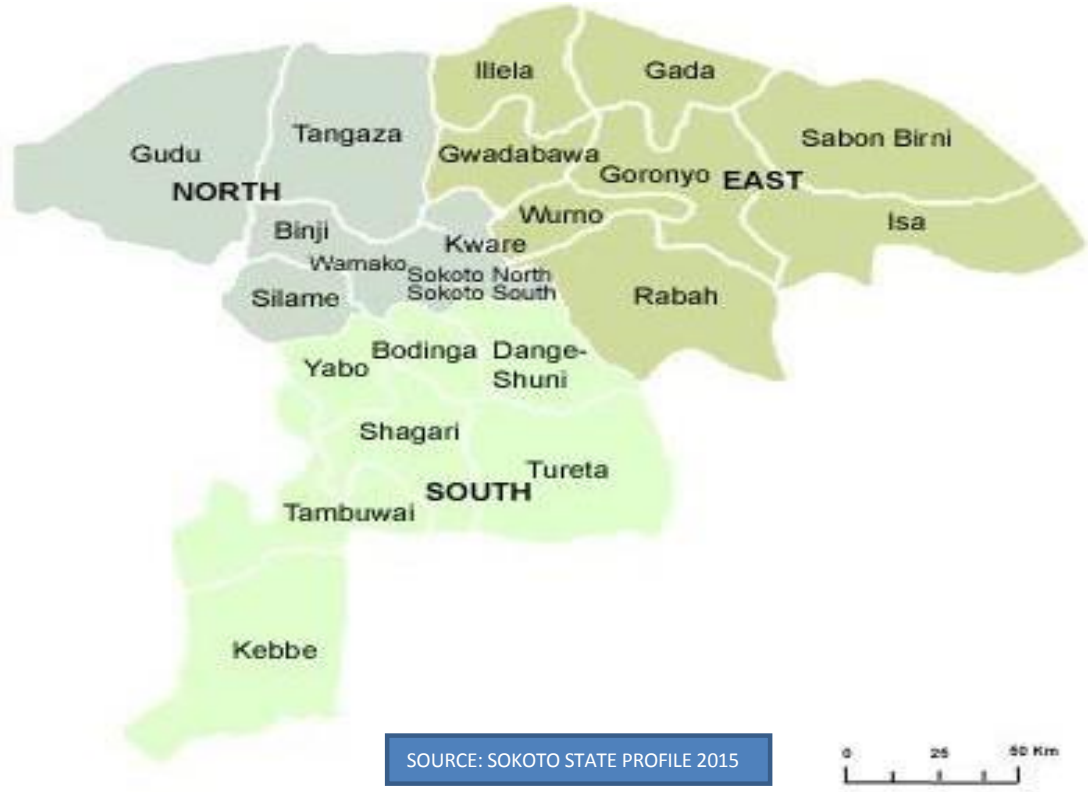

Figure 1. Map of Sokoto State in Nigeria.

Solid waste generated in many cities in Nigeria is composed of organic materials, plastics/polythene, cans/metals, bottles/glasses, clothes/shoes, and ceramics (Imoh and Udofia, 2005; Aliyu, 2010). Household waste have been found to also contain hazardous and toxic waste such as expired drugs, dried cells, broken class, syringes which constitute serious environmental and health hazards (Delgado et al., 2007).

Urban waste generation in Nigeria was reported to be in the range of 12,000 to 255,556 tons per month with Lagos, the commercial hub in the country, generating the highest followed by Kano (Ogwueleka, 2009). It is worthy to note that Lagos and Kano are the most populous state in Nigeria by 2006 National population Census. Population growth, increasing urbanization, changes in consumption pattern, and rapid developments in technology have all contributed to an increase in demand for goods and services which lead to introduction of different products to meet up with consumer need and demand (Odum and Odum, 2006). These factors together with lack of effective recycling activities resulted in an increase in both the quantity and the variety of solid wastes generated and disposed-off as waste.

The management of solid waste as important as it may disposal will affect the population's perception and willingness to participate in best waste management practices (Adekunle et al., 2012).

In Sokoto metropolis there is persistent littering of surrounding with household waste and other construction debris in manner best described as "throw it where you like" that now resulted to piles of refuse dotting the entire metropolis. This problems need to be addressed and on this background the study was conducted to determine the public opinion and perception on solid waste disposal method in the metropolis and to see whether the littering is related to the perception of the people of Sokoto metropolis.

MATERIALS AND METHODS

Sokoto is a capital of Sokoto State and located in the northwest region of the country Nigeria, within the latitude 12^0N and 13S, 58N and longitude 48W and 60-54E bounded in the north by Niger Republic, Zamfara State to the east and Kebbi State to the south be is a sole responsibility of Local Government Areas and west. It has land area of 26,648.48 km^2 (Figure 1) and (LGAs) in the country. Unfortunately this level of government is not technically and financially positioned to implement this function. Where some minimal efforts are made, it is characterized by the use of inappropriate technology, inadequate collection and

transportation systems as well as unsafe final disposal options. Thus, inability of local governments to manage municipal solid wastes result to heaps of refuse dotting in major roads and highways with associated environmental contamination and pollution (Longe and Kehinde, 2005). Household wastes in Nigeria, which are of different sources, are not segregated before disposal (Longe and Williams, 2006). This is better attributed to lack of integrated waste management system which promotes waste reduction, reuse and recycling activities. A similar condition is prevalent in Indian as reported by Chattopadhyaya et al. (2011) where household were not segregated coupled with poor waste collection system.

The perception of one's capability is said to set a limit to what to do and ultimately what can be achieved (Holland and Rosenberg, 1996). Perception influences how a person views himself and the world around him and how it tends to govern his behaviour. Dann Marie (2009) reported that residents' perception are positively correlated with solid waste management practices. This suggests that residents with positive environmental perception tend to perform responsible solid waste management which entailed waste collection and proper disposal.

Population perception of waste management describes the whole process of how the populace comes to know what is going on regarding best practices in waste management. Awareness and enlightenment programs through information, education (formal and informal), capacity building, coupled with implementation and execution of laws and regulations on proper waste population size of 3,696,999 (2006 national population census) with the metropolis being the most populous. The people of Sokoto are mainly Hausa and Fulani; others are Yoruba, Ibo, Zabarmawa, Nupe and some other tribes from other part of the country. The people of the state are mainly Muslim but Christianity is also practiced by some other tribes in the state. The vegetation is that of savannah zone with grass land suitable for cultivation of grains and animal husbandry. Many are engaged in farming and trading while also a significant proportion engaged in white collar job. Sokoto state has a mean annual rainfall of about 500 mm - 1,300 mm and temperature of 28.3°C.

A cross-sectional descriptive household survey design was used to explore public perception of refuse disposal in the Metropolis. The metropolis is made up of four local government areas (LGA) which included Sokoto North, Sokoto South, Part of Wamakko and Dange-Shuni. Each of these LGA consisted of ten political wards with each ward having number of settlements unevenly distributed. A total of nine hundred and two respondents participated in the survey. A multistage sampling technique was used to select the participants.

First, a simple random sampling method (balloting technique) was used to select five wards from each LGA. A list of all wards by local government areas in the metropolis was obtained and used as sampling frame. Secondly, from the each selected wards, five settlements were selected using simple random sampling method (Balloting technique). Third, a random sample of required size was allocated to each selected settlement using a stratified sampling method (proportional allocation technique) based on population distribution which resulted in unequal number of respondents being selected. Forth, using systematic sampling method, a number of compounds were selected based on proportion allocated to each selected settlement. From selected houses, a questionnaire was administered to the head of household, and where more than one household, a simple random sampling method (Balloting technique) was used to select one household head.

Data was collected by face to face interview using questionnaire that contained both open-ended and close-ended questions. Research assistants were drawn from the political wards selected for study and adequately trained to ensure adequacy and accuracy of the information to be collected during the interviews. After the training, research assistants were posted to their wards to administer the questionnaires.

Data collected was entered into and analyzed using Statistical Package for the Social Science (SPSS) version 17.0. The skewed quantitative data was summarized using Median and inter-quartile range while categorical variables using frequencies and percentages. The results were presented in tables and charts. Ethical approval to conduct the study was obtained from Sokoto State Health Research Ethics Committee and permission for community entry was granted by the District head of each of the selected ward. In addition, individual consent was obtained from the participants before the questionnaires were administered.

RESULTS

Table 1 showed that the respondents' median age was 30 years, IQR: 25- 43. There were more male (53%) respondents than females (47%). More than half (53%) had no formal education and among those that had formal education, only 18.3% completed secondary education while about 20% had tertiary education. Thirty five percent of the survey respondents were unemployed, 14% were traders and lecturers/mid-level business men, Top business men/civil servant made up 13% each. The majority ethnic group was Hausa (68.1%) while other minor ethnic groups accounted for 12.4% of the total. About one-third (30%) of the respondents had an estimated annual household income of less than N50,000 while 18% earned between N50,000 and N100,000 annually. A large proportion (57%) lived in houses with shared facilities while 43% lived in self-contained houses (flat, Bungalow or Story building).

Figure 2 showed that on the respondents' perception of sanitation situation in the state, of the eight hundred and forty three respondents, 94.1% feel worried how solid waste litters the metropolis. Among this proportion, 14.8% perceived it as a minor problem while 14% perceived it as a major problem.

Table 2 showed that 55% of the respondents reported that residents are responsible for the poor sanitation while 38% said government and 7% don't know who is responsible. For the cleaning of the surrounding, 41% of respondents said resident is responsible for cleaning their environment, 19% government and 40% said its responsibility of both government and the residents. Large number of respondents (63%) use children to dispose household refuse. majority of these children are from the household (59%) while 27% were Almajiris.

Table 3 showed that more than half (55%) of the respondents disposed their waste on an open field while30% burn their waste. Commonly used storage containers for house hold waste was old bucket (31%),

Table 1. Demographic and socio-economic characteristics of respondents.

Variables	Number (%)
Age groups (years)	
18-24	208 (23.1)
25-34	311 (34.5)
35-44	166 (18.4)
45-64	184 (20.4)
≥ 65	33 (3.7)
Sex	
Male	481 (53.4)
Female	419 (46.6)
Education level	
No formal education	474 (52.7)
Primary education	84 (9.4)
Secondary education	164 (18.3)
Tertiary education	174 (19.5)
Ethnic group	
Fulani	105 (11.3)
Hausa	633 (68.1)
Ibo	29 (3.1)
Yoruba	48 (5.2)
Others	115 (12.4)
Marital status	
Single	266 (29.2)
Married	582 (63.9)
Divorced	13 (1.4)
Widowed	50 (5.5)
Occupation	
Unemployed	314 (34.8)
Student	55 (6.1)
unskilled labourers	36 (4.0)
Trading/business	242 (26.8)
Skilled artisan	37 (4.1)
Civil servant	219 (24.3)
Respondents estimated annual household income	
<50,000	147 (30.0)
<100.000	89 (18.2)
<200,000	77 (15.7)
<500,000	65 (13.3)
<1,000,000	47 (9.6)
>1,000,000	65 (13.3)

Table 1. Contd.

Respondents type of houses	
Mud hut	88 (9.9)
Multiple hut unit	67 (7.6)
Mud house ± cement facing	121 (13.7)
Single room in a house shared by other household	142 (16.0)
Flat with shared facilities	172 (19.4)
Flat (self-contained)	193 (21.8)
Bungalow (self-contained)	85 (9.6)
Storey building (self-contained)	17 (1.9)

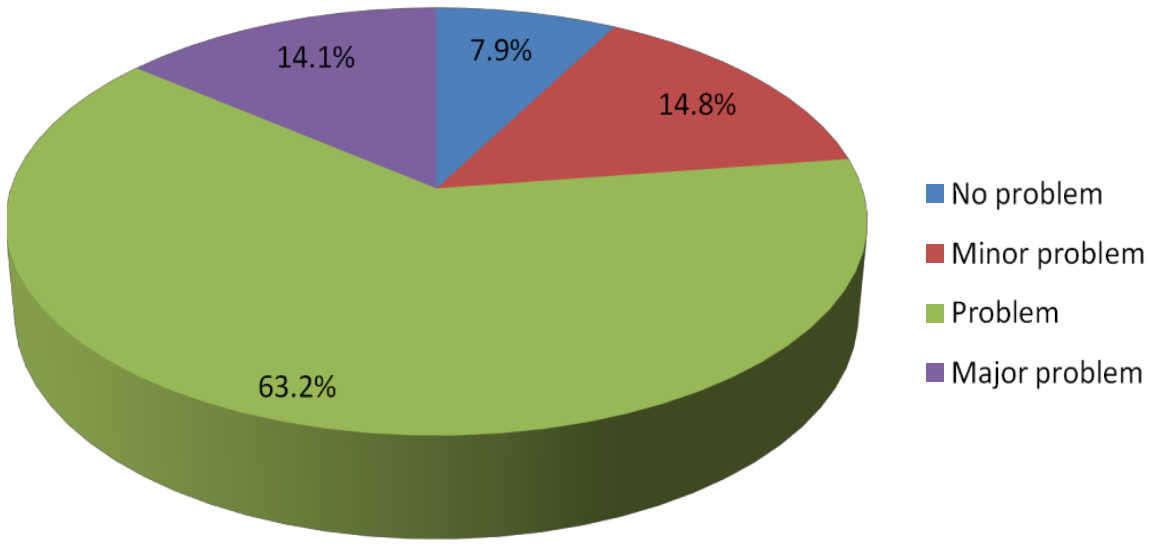

Figure 2. Respondents' perceptions of solid waste problems.

Table 2. Resident opinions on waste problem and handling responsibilities.

Variables	Number (%)
Feel worried how refuse litter the metropolis	
Yes	843 (94.1)
No	53 (5.9)
Who responsible for the problem of sanitation	
Residents	491 (55.4)
LGA	209 (23.6)
State	126 (14.2)
Don't know	61 (6.9)
Whose responsibility to clean surrounding	
Residents	315 (41.1)
Government	142 (18.5)
Both	310 (40.4)

Table 2. Contd.

Appropriate for resident to clean own surrounding	
Yes	845 (90.9)
No	51 (5.7)
Use children to dispose household refuse	
Yes	507 (62.6)
No	303 (37.4)
What category of children	
From household	383 (58.5)
From neighborhood	97 (14.8
Almajiris	175 (26.7)

Table 3. Household solid waste storage and disposal practice.

Variables	Number (%)
Storage containers for household waste	
Sacks	209 (25.3)
Plastic containers	175 (21.2)
Old bucket	257 (31.2)
Polythene bags	23 (2.8)
Waste bins	96 (11.6)
Waste bin with liners	36 (4.4)
Dump	29 (3.5)
Method of household waste disposal	
Burning	264 (30.2)
Burying	19 (2.2)
Open space dumping	483 (55.2)
Manuring	48 (5.5)
Government collected	61 (7.0)

while 3.5% of the respondents dump the waste on open field.

The chi-square analysis (Table 4) showed that only respondents' educational level (Fischer exact = 11.15, P= 0.02); awareness of associated health problems (Fischer exact = 5.10, P = 0.03); and feeling worried about dirty environment (X^2 = 194.78, df = 1, P = 0.001) demonstrated statistically significant association with their perception on waste disposal method.

Binary logistic regression analysis using forced entry method (table not shown) showed that only respondents' educational level demonstrated statistically significant association with their perception and thus did predict respondents' perception to waste disposal method in the metropolis (aOR =4.5, P = 0.001) and those with tertiary education (aOR = 2.5, p = 0.01). This means that respondents with tertiary education are about 2.5 times more likely express positive perception to the method of solid waste disposal in the metropolis.

DISCUSSION

Many approaches such as economic, engineering, scientific, environmental and behavioural have been used in the study of waste management. However, this study explores behavioural perspective with the view that the way people particularly manage waste is closely related to their attitude and perception. Individual perception is governed by past experience and present outlook, conditioned by values, moods, socials circumstances and individual expectation.

Within the household setting there exist distinctive division of labour between males and females. The

Table 4. Relationship between socio-demographic and related factors to respondents' perception of waste disposal practices.

Variables	Perception to waste disposal		
Age groups (years)	**Poor perception, n (%)**	**Good perception, n (%)**	**Test statistics and p value**
18-24	145 (21.6)	59 (27.3)	$X^2 = 3.19$, df =4, p =0.53
25-34	237 (35.3)	68 (31.5)	
35-44	124 (18.5)	39 (18.1)	
45-64	140 (20.9)	42 (19.4)	
≥ 65	25 (3.7)	8 (3.7)	
Sex			
Male	357 (52.9)	116 (54.0)	$X^2 = 0.07$, df =1, p =0.79
Female	318 (47.1)	99 (46.0)	
Educational level			
No formal education	358 (53.3)	113 (52.5)	Fischer exact = 11.15 P = 0.02*
Primary education	60 (8.9)	21 (9.8)	
Secondary education	133 (19.8)	31 (14.4)	
Tertiary education	120 (17.9)	50 (23.2)	
Ethnic group			
Fulani	83 (12.5)	20 (9.4)	Fischer exact = 2.99 P = 0.99
Hausa	470 (70.8)	154 (72.3)	
Ibo	22 (3.3)	7 (3.3)	
Yoruba	35 (5.3)	13 (6.1)	
Others	54 (8.2)	19 (8.8)	
Marital status			
Single	196 (28.8)	69 (31.4)	Fischer exact = 2.30 P = 0.51
Married	436 (64.0)	137 (62.3)	
Divorced	12 (1.8)	1 (0.5)	
Widowed	37 (5.4)	13 (5.9)	
Occupation			
Unemployed	239 (35.4)	73 (33.5)	Fischer exact = 5.61 P = 0.88
Student	44 (6.5)	11 (5.0)	
Unskilled labourers	20 (3.0)	14 (6.4)	
Trading/business	186 (37.5)	56 (25.7)	
Skilled artisan	30 (4.4)	7 (3.2)	
Civil servant	129 (19.1)	44 (20.2)	
Willingness to pay			
Yes	218 (41.4)	58 (34.9)	$X^2 = 2.23$, df = 1, p = 0.14
No	308 (58.6)	108 (65.1)	
Awareness of associated health problems			
Yes	290 (45.5)	87 (46.8)	Fischer exact = 5.10 P = 0.03*
No	347 (54.5)	99 (53.2)	
Worried about dirty environment			
Yes	695 (100)	148 (73.6)	
No	0	53 (26.4)	

*Significant at α error of 0.05.

current practice of household waste handling is considered and designated as women's responsibility however construction and demolition debris are considered man's responsibility. As part of proactive measures to protect public and the environment from the impact of the waste, the Nigerian Federal and state governments established various governmental authorities and agencies in addition to various statutory regulations guiding solid waste management in Nigeria that would ensure efficient and effective mode of waste management. These includes: National Environmental Standards and Regulations Enforcement Agency, Federal Ministry of Environment, State Ministries of Environment and State Environmental Protection Agencies (ELRI, 2009). The state also recently established task force for sanitation and illegal structures in order to promote clean and aesthetic environment.

Despite all these commitments, waste management in the country is still at primordial stage probably due to serious legal and policy gaps. Waste management system in developed nations with modern technologies, are maintained efficiently with minimal environmental impacts. However, in developing and yet to develop nations, poor waste management practices particularly in urban centres have been attributed to various environmental problems (Salhofer et al., 2008), (Ngoc and Schnitzer, 2009), (Rahji and Oloruntoba, 2009).

Observation during community walk-through revealed that there was no house to house waste collection and almost all the household waste is deposited at the dumps with no prior sorting and segregation. This indicated lack of formal waste management system in place with state employed cleaning companies also practicing the same. This observation is in tandem with report from Ijebu-ode, Nigeria where waste was observed to be left in piles for weeks around the dwellings most especially closer to the kitchen. These the study noted to create unaesthetically environmental condition (Banjo et al, 2009). Although a significant proportion of the resident expressed positive perception to the manner with which waste litter the whole metropolis however only very few perceived it as a serious problem. This study also revealed children involvement in the waste handling and disposal with large proportion admitting using children to dispose household waste onto the dumps and these children are largely from the household while Almajiris (children attending local islamiyya schools) also constituted another bulk of children involved in the household waste stream management. Poor implementation of international labour laws and child labour act promote the continuous use of underage children in waste collection and disposal services. Household wastes were found stored in different ways using inappropriate receptacles. There is no common or standard secured storage containers such as steel containers with secured lid as seen in some state and developed countries. The current storage facilities are prone to being scattered by scavenging animals and thus attract insects and vermins and some of the wastes are even spread around before getting to the dump site. This could be due to general poor perception of the problem and cost associated in obtaining standard containers. Study in southern Nigeria reported involvement of private waste managers by about 50% of the respondents, majority others used several unsanitary methods to get rid of the waste like dumping into gutter, burning, dumping on undeveloped land, while few others buried theirs (Banjo et al., 2009, George, 2008).

In order to improve solid waste management best practices, there is strong need for the government concerned to promote local community capacity through sensitization and awareness creation through campaigns, establish community waste management structure, support private partnership in waste collection and also organize well supervised community cleanup exercises.

Conclusion

Unsanitary solid waste disposal practice is still very popular in spite of documented associated health hazard. Even though large majority of residents expressed worries the manner waste dot the metropolis, only small minority perceived it as a major problem. There is need for government to introduce better waste containers replace what the majority of residents currently use.

Conflict of Interests

The authors hereby declared that there was no conflict of interest as it relates to the conduct; outcome of this research work and its publication.

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Full Length Research Paper

Environmental fate of pesticides applied on coffee crops in southeast of Brazil

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The aim of this paper was evaluate the environmental fate of pesticides applied in coffee crops in southeast of Brazil, using the level I fugacity model. Chemical and physical characteristics of the pesticides were considered in different environmental compartments and applied fugacity equations. The preliminary evaluation of contamination risk due the use of pesticides in coffee crops, using fugacity models, proved to be good tools to be used in the process of making decision to select pesticides with less impact on the environment, as well to prioritize the pesticides to be monitored. For most of the pesticides evaluated, the soil/sediment compartment was the most vulnerable.

Key words: Environmental fate, fugacity, organic micropollutants, pesticide.

INTRODUCTION

The benefits of pesticides are evident. However, the risk of adverse effects must be diminished. So, it is necessary to exert effective control of use and have available methods of calculating their environmental behavior.

The models employ calculations that use concepts of activity and fugacity to characterize the equilibrium that exists between environmental compartments. Most of the emphasis is on organic chemicals, which are more susceptible to generalization than inorganic chemical, when assessing environmental behavior (Mackay, 2001).

The best way to assess the pesticides impact potential in the environment consists of conducting field monitoring for a long period of time. However, this process requires high financial resources to produce consistent data.

The modeling is interesting to avoid unnecessary costs of residue analyses in vulnerable compartments. Nevertheless, none of these models consider the behavior of the compound in the soil and volatilization, leaching, superficial runoff and degradation process, simultaneously (Brooks and Roberts, 1999).

This study can contribute to predicting the environmental destination of pesticides and suggest the pollutants and compartments that must be investigated in monitoring programs. These models are interesting in the process of listing pesticides that present characteristics of environmental risks.

Mackay (2001) proposed a methodology to predict pesticides environmental destination, using fugacity

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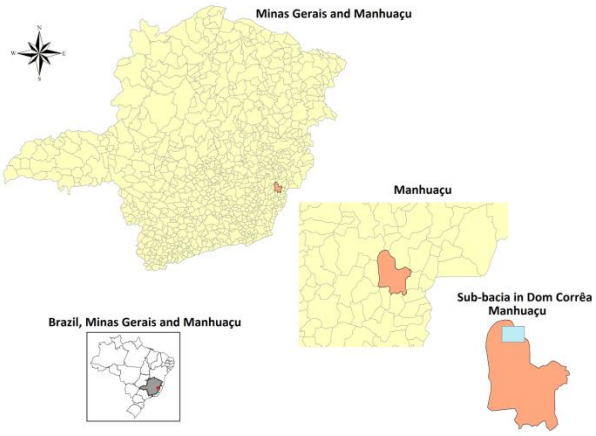

Figure 1. Localization of the study area.

concepts.

According to the author, fugacity can be the best way to quantify the transport, bioaccumulation and transference among different compartments (air, water, soil, sediment, biota, suspended solid and others). So, the model is proposed as a strategy to assess the environmental exposure to pesticides applied to crops. Based on fugacity, the model presents an estimate of concentration and partition in each compartment in the environment.

The application of fugacity concepts is convenient to chemical balance and partition calculations usually applied only in the last decades. Fugacity is also useful for describing mathematically the rates (pollutant quantities) in which chemical diffusion or transport occurs among phases. The transfer rate can be expressed as being proportional to the fugacity difference that exists between the source (origin) and the final phase (destiny). The mathematical procedures used in this methodology were developed from thermodynamic concepts, transport phenomena and kinetic reactions (Mackay, 2001; Mackay et al., 1997).

The model of fugacity has four complexity levels and is applied in environmental systems previously selected. The Level I calculates the pesticides distribution among compartments, considering thermodynamic balance of the partition coefficients in steady state.

This work use the model of fugacity Level I, due the available data to carry out the calculations. Thus, any degradations reactions and advance effects will not be taken into consideration.

The aim of the present work was to assess environmental destiny of pesticides, applied in coffee crops and marketed in Manhuaçu-MG, Brazil from 2007 to 2010, using fugacity models Level I. Some metabolites and pesticides detected in the surface water of sub-basin, situated in northern of Manhuaçu-MG, were also assessed to be checked with the results of the model.

MATERIALS AND METHODS

Study region

Manhuaçu is located in the Rio Doce hidrographic basin in Minas Gerais and highlights among other cities of the state, by its significant coffee production, more than 16,000 tons in 2014 (IBGE, 2016).

There are about 20 thousand coffee-producing properties in Manhuaçu region. This number represents 71% of the coffee-producing properties in the Zona da Mata, the second-largest coffee-producing region in the state. The local topography is mountainous, with altitudes ranging from 561 to 1,760 m. The average annual rainfall is 1,860 mm. Rainfall in the region, according to a field survey, occurs predominantly during the months of November through March (Soares et al., 2013). The rainy period is the same in the application of pesticides, increasing contamination of water and soil.

The most used pesticides in the study region are fungicides, herbicides and insecticides and are classified as non-mobile (Koc> 4000 $mL.g^{-1}$) or low mobility in the environment (500 <Koc <4.000 $mL.g^{-1}$), and according these characteristics, they are more prone to contamination of surface waters in the rainy season. Furthermore, it is necessary to highlight the characteristics of soils in the region – latosol – with thick and clayey layers. These characteristics favor runoff and reduce the risk of groundwater contamination, but increase the risk of surface water contamination.

The water source evaluated in this study was selected using multi-criteria analysis, as shown by Soares (2012). The sub-basin of the study in Dom Corrêa district is located in the upper-left corner of the polygon: X1= -42.17; Y1= -20.03; and, the lower right corner: X2= -42.10; Y2= -20.08 (Coordinates Lat. Long., WGS84), to the north of the city of Manhuaçu, according to presented Figure 1.

Study model

In this study, the mathematical model used applies concepts of fugacity, which was introduced by Lewis in 1901 as a more convenient thermodynamic equilibrium criterion than chemical potential. Its convenience in environmental chemical equilibrium or partitioning calculation has become apparent in only last three decades. This model shows that fugacity is useful to quantify mathematically the rates that chemicals diffuse or are transported between phases: for example volatilization of pesticides from soil to air. The transfer rate can be expressed as being led by, or proportional to, the fugacity difference that exists between the source and destination phases. Thus, this model express the behavior of the pesticides in the environment by: transforming chemical reaction, advective flow and nondiffusive transport rate equations into fugacity expressions and build up sets of fugacity equations describing the complex behavior of chemicals in multiphase. The steps by calculation of the equilibrium Level I distribution of a chemical are (Mackay, 2001):

1. Definition of the environment (volumes and compositions)
2. Input of relevant physical chemical properties
3. Calculation of Z values for each medium (Table 1)
4. Input of chemical amount (in this study, it was considered 1 mol)
5. Calculation of fugacity, and hence concentration, amounts, and percent distribution

The calculations were performed for 54 pesticides and metabolites of the three active ingredients of pesticides most used in coffee crops in Brazil (ETU; 1,2,4-triazole and endosulfan sulfate), totaling 57 substances.

Table 1. Definitions of Z values and equations used in Level I calculations.

Definitions of "Z" values
$Z_A = 1/RT$
$Z_w = 1/H = C^S/P^S = Z_A/K_{AW}$
$Z_o = Z_W K_{ow}$ (octanol)
$Z_P = 1/v_P P^S$ (pure phase)
$Z_S = y_{oc} K_{oc} Z_w (\rho_S/1000)$ (soils, sediments)
$K_{oc} = 0,41 K_{ow}$ (there are variations in this equation, as presented)
Where:
R: Gas constant (8,314 Pa.m³/mol K)
T: Absolute temperature (K)
H: HENRY´s law constant (Pa.m³.mol^{-1})
C^s: Solubility in water (mol.m^{-3})
P^s: Vapor pressure (Pa)
K_{AW}: Air-water partition coefficient
K_{ow}: Octanol-water partition coefficient
K_{oc}: Organic carbon-water partition coefficient
v_P: Molar volume of pure chemical (m³.mol^{-1})
y_{oc}: Mass fraction organic carbon
Note that the Z value is expressed by $Z_T = \Sigma v_i Z_i$; where v_i is the volume fraction of phase i.
Fugacity equation
$f = M/\Sigma V_i Z_i$
Where: f: fugacity (Pa); M: total amount of chemical (mol); V: volume (m³)
$C_i = Z_i f$; $m_i = C_i V_i = V_i Z_i f \therefore m_i$ is amount in phase i (mol)

Fonte: Mackay (2001).

The methodology presented by MACKAY (2001) and Excel® 10.0 (Office XP) software was used for the application of algorithms to each substance, according to equations presented in the Table 1. The method of evaluation describes the physic-chemical properties of pesticides assessed. The fugacity model Level I was used in this research, due the availability of data to apply the mathematic model.

Pesticides chemical properties used to calculate the potential of distribution in the environmental compartments were: molecular mass (M), vapour pressure at 25°C (VP), solubility in water at 20°C (S), Henry's law constant at 25°C (K_H), octanol water partition coefficient (K_{ow}), organic carbon water partition coefficient (K_{oc}), air-water partition constant (K_{AW}), soil-water partition constant (K_{SoW}) and sediment-water partition constant (K_{SeW}). The partition constants (K_{SoW} and K_{SeW}) were estimate by means of K_{oc} values, according to Mackay (2001). All necessary data to calculate potential pesticides distribution in the environment came from IUPAC database (IUPAC, 2016).

Level I model of fugacity was described in such a way that fugacity "f" is related to concentration "C" in mol.m^{-3}, by means of fugacity capacity "Z", given, in mol.m^{-3}.Pa^{-1} (MACKAY, 2001). Thus, one can calculate the concentration of a compound in a compartment by Equation 1.

$C = Z.f$ [Equation 1]

Where "f" is fugacity, given in Pascal units (Pa).

In this study, it is necessary to calculate the volumes the compartments considered in the environment, where the aim is to know pesticides dispersion. In this case, the compartments studied were: air, water, soil and sediment of a sub-basin located in northern Manhuaçu (called Dom Corrêa district sub-basin).

From the results of geoprocessing obtained by Soares et al. (2011), an approximate volume of 20 km^3 was selected, according to scheme presented in Figure 2. These volumes were calculated as follows:

1. Air volume: it was considered the topographical area of sub-basin Dom Corrêa district (16,933,086.48 m²) and the air located at an altitude of 1000 m, above the soil surface, according to Mackay (2001). This altitude is justified by the fact that the author reported that it is unlike that most of the pollutants can disperse in altitudes above the range of 500 to 2000 m. Thus, the air volume obtained was 1.69 x 10^{10} m³.
2. Water volume: the extension of watercourses located in the sub-basin is 37,015 m (Extension obtained from the vector measurement of the hydrographic network (two dimensions), with adjustment of 10%, to consider the terrain relief (three dimensions) the average width considered to waterways was 3.0 m and the maximum average depth of 1.0 m. Considering the transversal section of the streams as parabolic, these measures result in a volume of surface water in the sub-basin of 74,030 m³.
3. Sediment volume: the extent of watercourses located in the sub-basin is 37,015 m, considering the average width of the gutter of the streams equal 3.0 m, maximum average depth 1.0 m, sediment layer 3 cm, as suggested by Mackay (2001). From this data, a volume of sediment equal 3,331.35 m³ was obtained along the entire section of watercourses. For this calculation, the sediment being delimited between the two parables with vertices distant 3 cm

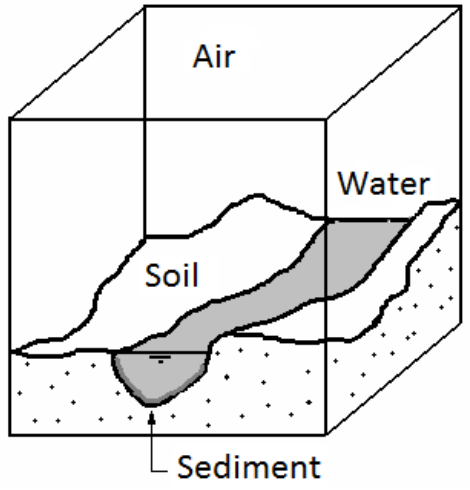

Figure 2. Schemetic representation of environmental compartments considered in this study.

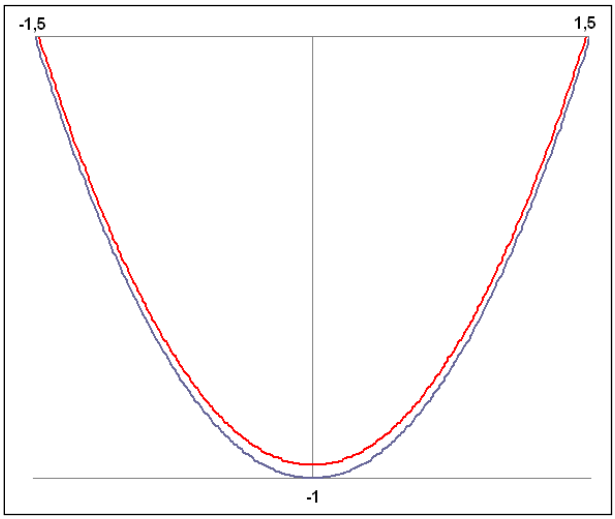

Figure 3. Parabolic section simulating streams gutter pipe (lower parable) and sediment layer (upper parable).

was considered, according to Figure 3. Thus, the volume of sediment in the sub-basin is 3331.35 m³.
4. Soil volume: taking into consideration the topographic area of the sub-basin (16.933.086,48 m²) and the soil situated 10 cm of depth, according to Mackay (2001), the soil volume considered in sub-basin is 1.693.308,65 m³.

The arithmetic average of the concentrations of organic carbon obtained for three different profiles of soil and seven sediment sampling sites, distributed along the sub-basin were calculated, as shown in Table 2. Thus, the values used in the calculations were the averages presented in Table 3.

In equifugacity state, Plese et al. (2009) explained that the compartments that have high fugacity capacity will have high concentrations of the compound. Thus, the authors reported that the fugacity capacity consists of a measure of the "solubility" of the compound in the compartment studied. Therefore, each compartment requires that its fugacity capacity be defined and that depends on physic-chemical properties of the compound and of the compartment nature studied. The fugacity capacities were calculated to each compartment by means of Equation 2.

$$C_i = Z_{ij}.f_i \quad (4) \qquad 2$$

Where: i = air (1); water (2); soil (3) and sediment (4). So, i = 1; 4 compartments; j = 1; 57 pesticides/metabolites.

In air, the fugacity of a compound (f_{ar}) is equal to its vapor pressure, expressed in terms of concentration, and is obtained by Equation 3:

$$F_{air} = C_{air}RT \qquad 3$$

Where: C_{air}, in mol.m^{-3}, is the concentration of the compound in the air; R = 8,314 Pa.m³.mol^{-1} and T is the absolute temperature in Kelvin degrees (*K*). Thus, the capacity of fugacity from the air (Z_{ar}) is given by Equation 4.

$$Z_{air} = \frac{1}{RT} \qquad 4$$

In water, the fugacity of a pesticide dissolved is roughly equivalent to its partial vapor pressure, described by Henry's Law, according to Equation 5.

$$f_{water} = HC_{water} \qquad 5$$

Where: f_{water} is the fugacity of the pesticide in water, expressed in Pa; H is the Henry's law constant (Pa.m³.mol^{-1}) and C_{water}, in mol m^{-3} is the concentration in the water. Thus, the capacity of the water fugacity (Z_{water}) is given by Equation 6:

$$Z_{water} = \frac{1}{H} \qquad 6$$

For soil and sediment compartments, the fugacity has no direct relation with the physico-chemical parameters of the compounds. This way, the capacity of fugacity "Z" to these compartments is obtained using the expression presented by Mackay (2001), according to Equation 7.

$$Z_{soil\ and\ sediment} = y_{oc}K_{oc}Z_{water}\frac{\rho_s}{1000} \qquad 7$$

Where: y_{oc} is the fraction of organic carbon (% OC); ρ_s is the density of soil or sediment (kg.m^{-3}). And the value "Z" of a phase was obtained by Equation 8:

$$Z_T = \Sigma\ V_iZ_i \qquad 8$$

V_i: is the volume fraction in phase "i" expressed in m³, the fugacity "f" in Pa, is given by Equation 9.

$$f = \frac{M}{\Sigma ViZi} \qquad 9$$

Table 2. Collection points for soil and sediment samples in Dom Corrêa sub-basin district of Manhuaçu

	Collection point	Coordinates geographical[1]	Description
Soil	Profile 1	0798228; 7780534	Under coffee crops. Altitude: 920m
	Profile 2	0799646; 7780426	
	Profile 3	0799839;7778527	Under coffee crops. Altitude: 950 m
Sediment	Sed 1	796811;7780716	Stream João Bento
	Sed 2	797127;7780925	
	Sed 3	798312;7780730	
	Sed 4	798966;7780626	
	Sed 5	799121;7780858	Tributary stream João Bento
	Sed 6	799399;7779540	Stream Bom Jardim
	Sed 7	799269;7778794	

[1]Datum SAD69.

Table 3. Contents of organic carbon (OC) and densities (Ds) obtained for samples of soil and sediment collected in the Dom Corrêa sub-basin.

	Point	OM[1] (dag.kg^{-1})	OC (dag kg^{-1})	Ds (g.cm^{-3})
Soil	Profile 1	3.45	2.00	1.36
	Profile 2	1.97	1.14	1.33
	Profile 3	2.34	1.36	1.11
	Average	**2.59**	**1.50**	**1.27**
Sediment	Sed 1	2.84	1.65	1.40
	Sed 2	1.47	0.85	1.60
	Sed 3	2.19	1.27	1.70
	Sed 4	2.31	1.34	1.50
	Sed 5	4.33	2.51	-
	Sed 6	3.67	2.13	1.45
	Sed 7	4.76	2.76	-
	Average	**3.08**	**1.79**	**1.53**

[1]Organic matter (OM) = Organic carbon (OC) x 1,724 – Walkley-Black. Source: Cunha (2011).

Where M is the total amount of pesticides (mol). The concentration in each phase (Ci) is calculated by Equation 10:

$$C_i = Z_i f \quad (10)$$

And the amount in each compartment (m_i) was obtained using Equation 11:

$$m_i = C_i V_i = V_i Z_i f \quad (11)$$

RESULTS AND DISCUSSION

Environmental fate of pesticides applied in coffee crops

The assessment of the environmental destination of pesticides, was performed in a relatively simple way through physic-chemical properties of the compounds, characteristics of the environmental compartments (content organic carbon and density), using the fugacity model Level I.

Considering the hydrographic sub-basin of study, the soil was the environmental compartment that showed the greatest vulnerability and disposition in the distribution of pesticides and some metabolites. Only acephate and methamidophos were predominant in water compartment, according to Table 4.

Thus, the surface water source contamination of the region of study is related to contamination by the carriage of contaminated soil with pesticides in rainy seasons. Concerning the concentration of pesticides in

Table 4. Percentage of pesticide in each compartment.

Pesticide/metabolites	Percentage (%) in compartments				Predominance
	Air	Water	Soil	Sediment	
Endosulfan sulfate*	6.30E-01	2.27E-01	9.89E+01	2.80E-01	Soil
ETU*	5.77E-06	4.40E-02	9.97E+01	2.82E-01	Soil
1,2,4-triazole*	2.64E+01	1.85E+00	7.16E+01	2.02E-01	Soil
2,4-D	4.71E-03	3.93E+00	9.58E+01	2.71E-01	Soil
Abamectin	1.01E-02	4.06E-02	9.97E+01	2.82E-01	Soil
Acephate	2.61E-04	5.34E+01	4.65E+01	1.32E-01	Water
Acetamiprid	2.72E-02	7.19E-01	9.90E+01	2.80E-01	Soil
Ametryn**	2.72E-02	7.19E-01	9.90E+01	2.80E-01	Soil
Atrazine**	3.10E-02	2.24E+00	9.75E+01	2.76E-01	Soil
Azoxystrobin	3.63E-07	5.38E-01	9.92E+01	2.81E-01	Soil
Benalaxyl	2.75E-02	4.58E-02	9.96E+01	2.82E-01	Soil
Cyhexatin	9.67E-02	5.24E-02	9.96E+01	2.82E-01	Soil
Cypermethrin	4.94E-03	2.67E-03	9.97E+01	2.82E-01	Soil
Cyproconazole	2.69E-03	5.83E-01	9.91E+01	2.80E-01	Soil
Cyromazine	2.98E-07	5.56E-01	9.92E+01	2.80E-01	Soil
Clethodim	1.75E-03	5.41E+00	9.43E+01	2.67E-01	Soil
Chlorfenapyr	1.02E-03	1.91E-02	9.97E+01	2.82E-01	Soil
Chlorpyrifos**	1.22E+00	2.77E-02	9.85E+01	2.79E-01	Soil
Deltametrin**	6.40E-05	2.24E-05	9.97E+01	2.82E-01	Soil
Difenoconazole	8.42E-06	6.08E-02	9.97E+01	2.82E-01	Soil
Diuron	3.95E-05	2.14E-01	9.95E+01	2.81E-01	Soil
Endosulfan Total	2.65E+00	1.94E-02	9.71E+01	2.75E-01	Soil
Enxofre	5.38E-01	1.17E-01	9.91E+01	2.80E-01	Soil
Epoxiconazole**	9.25E-03	2.13E-01	9.95E+01	2.81E-01	Soil
Esfenvalerate	1.95E-03	4.32E-02	9.97E+01	2.82E-01	Soil
Famoxadone	2.60E-02	6.11E-02	9.96E+01	2.82E-01	Soil
Fenoxaprop-p-ethyl	5.10E-04	2.02E-02	9.97E+01	2.82E-01	Soil
Fenpropathrin**	4.35E+01	2.59E-02	5.64E+01	1.59E-01	Soil
Fipronil	8.42E-03	3.95E-01	9.93E+01	2.81E-01	Soil
Fludioxonil	1.52E-05	3.05E-03	9.97E+01	2.82E-01	Soil
Flutriafol**	1.04E-04	8.89E-01	9.88E+01	2.80E-01	Soil
Fomesafen	8.08E-05	4.38E+00	9.54E+01	2.70E-01	Soil
Indoxacarb	1.97E-04	3.55E-02	9.97E+01	2.82E-01	Soil
Malathion	9.63E-02	1.04E+00	9.86E+01	2.79E-01	Soil
Mancozeb	1.25E-02	2.29E-01	9.95E+01	2.81E-01	Soil
Metalaxyl-M	1.12E-03	3.46E-01	9.94E+01	2.81E-01	Soil
Methamidophos	1.03E-02	6.96E+01	3.03E+01	8.58E-02	Water
Methomyl	1.64E-03	8.33E+00	9.14E+01	2.59E-01	Soil
Metolachlor	2.03E-01	1.00E+00	9.85E+01	2.79E-01	Soil
Metribuzin	1.05E-02	5.68E+00	9.40E+01	2.66E-01	Soil
Novaluron	4.22E+00	2.28E-02	9.55E+01	2.70E-01	Soil
Oxytetracycline	3.54E-21	2.23E-03	9.97E+01	2.82E-01	Soil
Pencycuron	1.86E-06	4.04E-02	9.97E+01	2.82E-01	Soil
Permethrin	3.99E-02	2.29E-03	9.97E+01	2.82E-01	Soil
Picloram	1.70E-04	6.14E+00	9.36E+01	2.65E-01	Soil
Pyraclostrobin	1.02E-05	2.08E-02	9.97E+01	2.82E-01	Soil
Pyriproxyfen	1.16E-02	1.08E-02	9.97E+01	2.82E-01	Soil
Profenofos	1.73E-02	1.13E-01	9.96E+01	2.82E-01	Soil

Table 4. Contd.

Propanil	9.14E-03	5.69E-01	9.91E+01	2.80E-01	Soil
Simazine	8.94E-03	1.73E+00	9.80E+01	2.77E-01	Soil
Spinosad	1.15E-07	6.61E-03	9.97E+01	2.82E-01	Soil
Tebuconazole	2.74E-04	2.97E-01	9.94E+01	2.81E-01	Soil
Teflubenzuron	5.66E-03	8.78E-03	9.97E+01	2.82E-01	Soil
Thiobencarb	7.25E-01	2.13E-01	9.88E+01	2.79E-01	Soil
Triadimenol	2.69E-04	8.31E-01	9.89E+01	2.80E-01	Soil
Triazophos	2.87E-01	6.33E-01	9.88E+01	2.79E-01	Soil
Trifloxystrobin	2.04E-02	9.62E-02	9.96E+01	2.82E-01	Soil

(*) Metabolites; (**) these pesticides were also detected in chromatographic semi-quantitative assays of surface water in the study region (Streams João Bento and Bom Jardim).

Table 5. Concentration of pesticides in the compartments.

Pesticides/metabolites	Concentration (µg.L^{-1}) in the compartments				Predominance
	Air	Water	Soil	Sediment	
Endosulfan sulfate*	8.79E-10	7.26E-05	1.38E-03	1.98E-03	Sediment
ETU*	3.33E-14	5.82E-05	5.76E-03	8.28E-03	Sediment
1,2,4-triazole*	2.26E-07	3.61E-03	6.12E-03	8.80E-03	Sediment
2,4-D	1.26E-11	2.40E-03	2.56E-03	3.68E-03	Sediment
Abamectin	6.89E-12	6.32E-06	6.79E-04	9.76E-04	Sediment
Acephate	8.42E-13	3.94E-02	1.50E-03	2.16E-03	Water
Acetamiprid	7.07E-11	4.28E-04	2.57E-03	3.70E-03	Sediment
Ametryn**	7.08E-11	4.28E-04	2.57E-03	3.70E-03	Sediment
Atrazine**	8.48E-11	1.40E-03	2.67E-03	3.84E-03	Sediment
Azoxystrobin	5.31E-16	1.80E-04	1.45E-03	2.09E-03	Sediment
Benalaxyl	4.98E-11	1.90E-05	1.81E-03	2.60E-03	Sediment
Cyhexatin	1.48E-10	1.84E-05	1.53E-03	2.19E-03	Sediment
Cypermethrin	7.00E-12	8.68E-07	1.41E-03	2.03E-03	Sediment
Cyproconazole	5.45E-12	2.70E-04	2.01E-03	2.88E-03	Sediment
Cyromazine	1.06E-15	4.52E-04	3.52E-03	5.07E-03	Sediment
Clethodim	2.87E-12	2.03E-03	1.55E-03	2.22E-03	Sediment
Chlorfenapyr	1.48E-12	6.32E-06	1.44E-03	2.08E-03	Sediment
Chlorpyrifos**	2.06E-09	1.07E-05	1.66E-03	2.38E-03	Sediment
Deltametrin**	7.48E-14	5.98E-09	1.17E-03	1.68E-03	Sediment
Difenoconazole	1.22E-14	2.02E-05	1.45E-03	2.08E-03	Sediment
Diuron	1.00E-13	1.24E-04	2.52E-03	3.62E-03	Sediment
Endosulfan Total	3.84E-09	6.43E-06	1.41E-03	2.03E-03	Sediment
Enxofre	9.91E-09	4.91E-04	1.82E-02	2.62E-02	Sediment
Epoxiconazole**	1.66E-11	8.72E-05	1.78E-03	2.56E-03	Sediment
Esfenvalerate	2.75E-12	1.39E-05	1.40E-03	2.02E-03	Sediment
Famoxadone	4.10E-11	2.21E-05	1.57E-03	2.26E-03	Sediment
Fenoxaprop-p-ethyl	8.32E-13	7.52E-06	1.63E-03	2.34E-03	Sediment
Fenpropathrin**	7.35E-08	1.00E-05	9.52E-04	1.37E-03	Sediment
Fipronil	1.14E-11	1.22E-04	1.34E-03	1.93E-03	Sediment
Fludioxonil	3.62E-14	1.66E-06	2.37E-03	3.41E-03	Sediment
Flutriafol**	2.04E-13	3.99E-04	1.94E-03	2.78E-03	Sediment
Fomesafen	1.09E-13	1.35E-03	1.28E-03	1.85E-03	Sediment
Indoxacarb	2.20E-13	9.08E-06	1.12E-03	1.60E-03	Sediment

Table 5. Contd.

Malathion	1.72E-10	4.26E-04	1.76E-03	2.53E-03	Sediment
Mancozeb	2.71E-11	1.14E-04	2.17E-03	3.11E-03	Sediment
Metalaxyl-M	2.36E-12	1.67E-04	2.10E-03	3.02E-03	Sediment
Methamidophos	4.30E-11	6.66E-02	1.27E-03	1.82E-03	Water
Methomyl	5.96E-12	6.93E-03	3.33E-03	4.78E-03	Water
Metolachlor	4.23E-10	4.76E-04	2.05E-03	2.95E-03	Sediment
Metribuzin	2.89E-11	3.58E-03	2.59E-03	3.73E-03	Sediment
Novaluron	5.05E-09	6.26E-06	1.14E-03	1.65E-03	Sediment
Oxytetracycline	4.54E-30	6.54E-07	1.28E-03	1.84E-03	Sediment
Pencycuron	3.35E-15	1.66E-05	1.79E-03	2.57E-03	Sediment
Permethrin	6.02E-11	7.90E-07	1.50E-03	2.16E-03	Sediment
Picloram	4.16E-13	3.43E-03	2.29E-03	3.29E-03	Water
Pyraclostrobin	1.55E-14	7.25E-06	1.52E-03	2.18E-03	Sediment
Pyriproxyfen	2.13E-11	4.54E-06	1.83E-03	2.63E-03	Sediment
Profenofos	2.73E-11	4.10E-05	1.57E-03	2.26E-03	Sediment
Propanil	2.47E-11	3.52E-04	2.68E-03	3.86E-03	Sediment
Simazine	2.62E-11	1.16E-03	2.87E-03	4.13E-03	Sediment
Spinosad	9.22E-17	1.21E-06	7.97E-04	1.15E-03	Sediment
Tebuconazole	5.26E-13	1.30E-04	1.91E-03	2.74E-03	Sediment
Teflubenzuron	8.77E-12	3.11E-06	1.55E-03	2.22E-03	Sediment
Thiobencarb	1.66E-09	1.12E-04	2.26E-03	3.25E-03	Sediment
Triadimenol	5.36E-13	3.80E-04	1.97E-03	2.84E-03	Sediment
Triazophos	5.40E-10	2.73E-04	1.86E-03	2.68E-03	Sediment
Trifloxystrobin	2.95E-11	3.18E-05	1.44E-03	2.07E-03	Sediment

(*) Metabolites; (**) these pesticides were also detected in semi-quantitative chromatographic assays surface water of the study area (Streams João Bento and Bom Jardim).

compartments, that is, without considering the volume of each of these compartments, it can be noted in Table 5 that the sediment is the predominant compartment, except acephate, methamidophos, methomyl and picloram that were predominat in water.

Environmental fate of pesticides found in the surface waters of the hydrographic sub-basin study

Considering the pesticides found in the waters of the sub-basin study by GC/MS-MS and LC/MS-MS, according to Soares et al. (2013), the soil was the environmental compartment that presented the greatest vulnerability and disposition in the distribution of pesticides according Table 6.

This Table 6 presents the percentage amount of pesticide in compartments. One notes that only heptachlor, mirex and terbufos presented predominance in the air. The results indicate that the contamination of the waters may be attributed to the carriage of contaminated soil during the rainy season and favored by mountainous relief, predominant in the area of study, as well as the illegal occupation by crops in the banks of watercourses that should be destined to permanent preservation, according to Brazilian Forest Code.

The results indicated predominance of pesticides in the air, their occurrence in surface waters which may be due to rainfall. These results agree with those presented by estimating the risk of contamination of surface and ground water, using Goss and GUS criteria, respectively and presented by Soares et al. (2012).

Regarding the concentration of pesticides in compartments, the predominance of these substances occurred in the sediment (Table 7). However, after pluvial precipitation, suspended solids with pesticides absorbed, as well as the revolving of sediments of watercourses provide the highest concentration of pesticides in these periods in the water.

Thus, terbufos was found in the waterways of Manhuaçu (Soares, 2013). European Union classification reports that terbufos is “very toxic to aquatic life with long

Table 6. Percentage quantity of pesticides in the compartments.

Pesticide	Quantity (%) in the compartments				
	Air	Water	Soil	Sediment	Predominance
Ametryn	2.72E-02	7.19E-01	9.90E+01	2.80E-01	Soil
Atrazine	3.10E-02	2.24E+00	9.75E+01	2.76E-01	Soil
Bifenthrin	6.91E-06	9.67E-04	9.97E+01	2.82E-01	Soil
Cyfluthrin	9.03E-03	1.85E-03	9.97E+01	2.82E-01	Soil
Clorpirifos	1.22E+00	2.77E-02	9.85E+01	2.79E-01	Soil
DDT	1.18E-01	1.51E-03	9.96E+01	2.82E-01	Soil
Deltamethrin	6.40E-05	2.23E-05	9.97E+01	2.82E-01	Soil
Ethion	8.13E-02	2.29E-02	9.96E+01	2.82E-01	Soil
Epoxiconazole	9.25E-03	2.13E-01	9.95E+01	2.81E-01	Soil
Fenvalerate	1.68E-01	4.33E-02	9.95E+01	2.81E-01	Soil
Fenpropathrin	4.35E+01	2.59E-02	5.64E+01	1.59E-01	Soil
Flutriafol	1.04E-04	8.89E-01	9.88E+01	2.80E-01	Soil
Heptachlor	7.57E+01	2.32E-03	2.43E+01	6.87E-02	Air
L-cyhalotrin	2.35E-03	1.27E-03	9.97E+01	2.82E-01	Soil
Metolachlor	2.50E-01	1.13E+00	9.83E+01	2.78E-01	Soil
Metoxychlor	5.28E-03	2.86E-03	9.97E+01	2.82E-01	Soil
Mirex	9.68E+01	1.25E-03	3.15E+00	8.92E-03	Air
Permethrin	3.99E-02	2.29E-03	9.97E+01	2.82E-01	Soil
Pirimicarb	1.12E-02	3.67E+00	9.60E+01	2.72E-01	Soil
Pirimiphos ethyl	2.40E+01	5.75E-01	7.52E+01	2.13E-01	Soil
Pirimiphos methyl	1.17E-03	2.08E-01	9.95E+01	2.81E-01	Soil
Propargite	3.37E-01	5.70E-02	9.93E+01	2.81E-01	Soil
Temephos	4.20E-05	2.29E-03	9.97E+01	2.82E-01	Soil
Terbufos	5.32E+01	2.13E-01	4.65E+01	1.31E-01	Air

Table 7. Concentration of pesticides in compartments.

Pesticides	Concentration ($\mu g.m^{-3}$) in compartments				
	Air	Water	Soil	Sediment	Predominance
Ametryn	7.08E-11	4.28E-04	2.57E-03	3.70E-03	Sediment
Atrazine	8.48E-11	1.40E-03	2.67E-03	3.84E-03	Sediment
Bifenthrin	9.65E-15	3.09E-07	1.39E-03	2.00E-03	Sediment
Cyfluthrin	1.23E-11	5.74E-07	1.36E-03	1.95E-03	Sediment
Clorpyrifos	2.06E-09	1.07E-05	1.66E-03	2.38E-03	Sediment
DDT	1.96E-10	5.77E-07	1.66E-03	2.39E-03	Sediment
Deltamethrin	7.48E-14	5.98E-09	1.17E-03	1.68E-03	Sediment
Ethion	1.25E-10	8.03E-06	1.53E-03	2.20E-03	Sediment
Epoxiconazole	1.66E-11	8.72E-05	1.78E-03	2.56E-03	Sediment
Fenvalerate	2.36E-10	1.39E-05	1.40E-03	2.01E-03	Sediment
Fenpropathrin	7.35E-08	1.00E-05	9.52E-04	1.37E-03	Sediment
Flutriafol	2.04E-13	3.99E-04	1.94E-03	2.78E-03	Sediment
Heptachlor	1.20E-07	8.40E-07	3.84E-04	5.52E-04	Sediment
L-cyhalothrin	3.08E-12	3.82E-07	1.31E-03	1.88E-03	Sediment
Metolachlor	5.20E-10	5.37E-04	2.05E-03	2.94E-03	Sediment
Metoxychlor	9.02E-12	1.12E-06	1.70E-03	2.45E-03	Sediment
Mirex	1.05E-07	3.09E-07	3.42E-05	4.91E-05	Sediment
Permethrin	6.02E-11	7.90E-07	1.50E-03	2.16E-03	Sediment

Table 7. Contd.

Pirimicarb	2.77E-11	2.08E-03	2.38E-03	3.42E-03	Sediment
Pirimiphos ethyl	4.64E-08	2.55E-04	1.45E-03	2.09E-03	Sediment
Pirimiphos methyl	2.25E-12	9.18E-05	1.92E-03	2.77E-03	Sediment
Propargite	5.67E-10	2.20E-05	1.67E-03	2.41E-03	Sediment
Temephos	5.32E-14	6.63E-07	1.26E-03	1.81E-03	Sediment
Terbufos	1.09E-07	9.99E-05	9.52E-04	1.37E-03	Sediment

lasting effects".

Conclusions

In terms of concentration of the pesticides in the environment and without considering the volume of the compartments, the modeling studies (Fugacity Level I) indicated the predominance of the pesticides in the sediment. Already in terms of percentage and considering the volume of the compartments, the predominance of the pesticides was in the soil. Thus, for most of the pesticides evaluated, the sediment and soil compartment was the most vulnerable.

The model using concepts of fugacity, applied in this work, showed good tool for use in the process of decision to select pesticides that have less environmental impact, as well as prioritization process of the compounds to be monitored. It is emphasized, however, the importance of applying other levels of modeling (fugacity), considering environmental conditions, where there are: advection, degradation, emission and transfer of substance between compartments.

This modeling was proper when compared with results of chromatographic assays of surface water collected in hydrographic sub-basin of study.

Conflict of interests

The author has not declared any conflict of interests.

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Full Length Research Paper

Effect of degradation on microbiological and physiochemical parameters of domestic wastewaters from the Federal University of Technology, Akure, Nigeria

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Domestic wastewater from ten (10) different residential halls in the Federal University of Technology, Akure were collected and analyzed by considering microbiological and physiochemical characteristics and their degradation with time. Pour plating technique was used for the microbiological analysis, physico-chemical parameters were assayed using the American Public Health Association methods, while degradation was non-synthetic. The rates of degradation, changes in physicochemical parameters as well as the microbial composition were studied using standard methods. The result showed that all the samples were heavily populated with microorganisms, having microbial load of 1.86 x 10^7 cfu/ml. The coliform was highest in sample from Akindeko hostel with a microbial load of 1.85 x 10^7 cfu/ml. A total of sixteen bacterial isolates were identified among which are *Proteus vulgaris*, *Shigella dysenteriae*, *Serratia marcescens* and *Clostridium botulinum.* Eight fungi were isolated with *Aspergillus flavus* predominating. The pH values were all alkaline ranging from 7.10 to 9.20. The dissolved oxygen decreased with increased days of degradation. Conductivity of the wastewater also increased with days of degradation while the total dissolved solid decreased with increased days of degradation. Mineral analysis showed decrease in all the samples with increase in days of degradation. The studied wastewaters are therefore toxic and should not be discharged into water bodies without adequate treatment and certification of their safety level microbiologically.

Key words: Akure, residential halls, wastewater, physico-chemical, degradation, microbiological.

INTRODUCTION

Steady growth in the number of students admitted into the Federal University of Technology, Akure (FUTA) (Adebisi et al., 2015) subsequently indicates steady increase in generation of domestic wastewater from each

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of the residences accommodating the students. The wastewaters generated from these residences are discharged without treatment directly into the environment. Municipal wastewater contains a variety of inorganic substances from domestic and industrial sources which include a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury and zinc (Mara, 2003). High levels of biochemical oxygen demand (BOD) and a reduction in dissolved oxygen which is as a result of biodegradable organic matter in receiving waters is detrimental to aquatic life. This is due to high competition for oxygen within the ecosystem (Ogbomida et al., 2016). Nutrients (nitrogen and phosphorus) enrichment in receiving sensitive bodies of water can cause eutrophication by stimulating the growth of algae (called an algal bloom) (Ogbomida et al., 2016). Blooming and finally collapse of algae may lead to hypoxia/anoxia and hence mass mortality of benthic invertebrates and fish over large areas (Wu, 1999; Foroughi et al., 2010) due to aquatic dissolved oxygen depletion. In advance, biodegradability tests need to be carried out in laboratory; this is to verify possibility of treating the wastewater biologically before it is released back to a body of water. This study aims at assessing the effect of the degradation process on microbiological and physiochemical parameters of domestic wastewater generated in University residential areas.

MATERIALS AND METHODS

Sample collection

The domestic wastewater samples were collected from ten (10) different residential halls within and outside the Federal University of Technology, Akure. The halls include Akindeko, Abiola, Jibowu, Annex, and Postgraduate hostels and the senior staff and junior staff quarters. Wastewater was collected in sterile 500 ml sample bottles according to standard methods of Cheesbrough (2006) for microbiological analysis. Two litres of domestic wastewater samples were also collected in clean sterile plastic containers and transported for physico-chemical analysis. The water samples were collected with the bottles facing upward and underneath stream towards the flow of water to avoid contamination (Cheesbrough, 2006). The collection was made in the morning hours when more wastewaters are usually generated and transported immediately to the laboratory within 4 to 6 h after collection for analysis. These samples were used for day 0; before commencement of degradation.

Degradation of wastewater samples

Five litres of domestic wastewater were collected from different locations in clean sterile containers. These were subjected to natural degradation for 32 days during which physico-chemical parameters and microbial isolation were carried out every 7 days.

Preparation of culture media

The following media was used for this study: nutrient agar and MacConkey agar. The agars were prepared according to manufacturer's instructions.

Enumeration of microorganisms from sample sources

Serial dilution of each of the collected wastewater samples was carried out to a dilution factor of 10^4 and 0.1 ml aliquot was pipetted into sterile Petri dishes. Sterile agars were aseptically poured into inoculated Petri dishes. The plates were incubated in an inverted position at 37°C for 24 h, while plates for the isolation of fecal coliforms were incubated at 44°C for 24 h. The control of each batch of the test medium was confirmed by incubating one un-inoculated plate along with the inoculated plates. The coliforms and total mesophilic bacteria counts were enumerated on MacConkey and Nutrient agar, respectively.

Isolation and identification of isolates

Representative colonies of bacteria were picked from various plates after incubation. Pure cultures of isolates were obtained with the aid of streaking discrete and different morphological typed colonies on freshly prepared nutrient agar plates. The agar plates were duly incubated. The resulting distinct colonies were used for succeeding characterization tests. Bacterial isolates were identified in accordance with the schemes of the Bergey's Manual of Determinative Bacteriology (Holt et al., 1994). The identified bacteria were maintained on nutrient agar respectively, slanted at 4°C in refrigerator for subsequent use.

Determination of parameters of wastewater

Physico-chemical parameters of wastewater samples such as the dissolved oxygen (DO), pH, total suspended solids, total dissolved solids, temperature, conductivity, turbidity, biochemical oxygen demand (BOD) were determined using the methods of Ademoroti (1996) and APHA (1998).

Data analysis

Variations in day intervals in relation to the physicochemical and microbial conditions were statistically measured. Data obtained were analyzed by one way analysis of variance (ANOVA) and means were compared by Duncan multiple range test (DMRT) using SPSS 18.0 version. Differences were considered significant at $P \leq 0.05$.

RESULTS AND DISCUSSION

Isolation and identification of microorganisms

The results of the bacterial load of isolated micro-organisms from domestic wastewater are shown in Figure 1. All the samples were heavily populated on day one, with the highest value recorded in Jibowu hall wastewater having 18.6×10^6 cfu/ml and the least was found in Annex Hall wastewater with 12.0×10^6 cfu/ml. However, there was reduction in the microbial load alongside the days of degradation with the least found in Akindeko hall with 1.8×10^6 cfu/ml on day 32. Figure 1

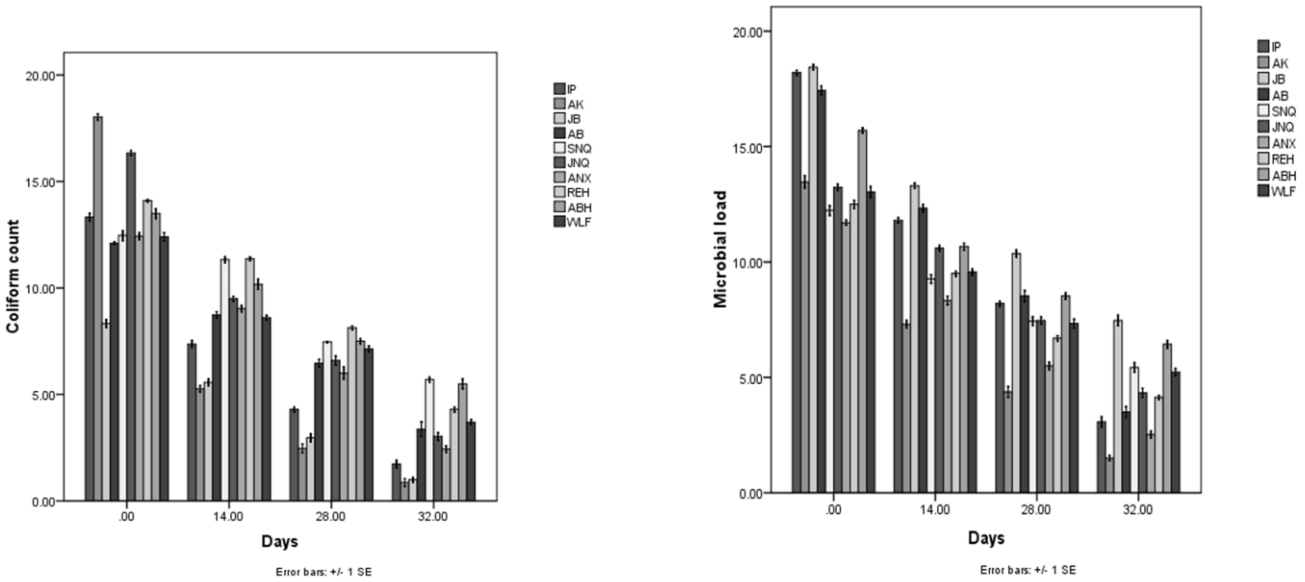

Figure 1. Microbial load (top left) and coliform count (top right) of isolated microorganisms from domestic wastewater samples (cfu/ml).

also shows the result of the coliform count isolated from the domestic wastewater. This follows similar trend as the microbial load isolated, with the highest isolation found in Akindeko hall wastewater with 18.5 x 10^6 cfu/ml and the lowest in Jibowu hall wastewater with 8.3 x 10^6 cfu/ml on day 1, reduction was noticed with the day of degradation with the least count in Akindeko hall wastewater on day 32 with 1.3 x 10^6 cfu/ml.

The identified bacteria as shown in Table 1 include *Staphylococcus aureus, Serratia marcenscens, Proteus vulgaris, Shigella dysenteriae, Bacillus substilis, Escherichia coli, Streptococcus faecalis, Klebsiella pneumonia, Pseudomonas aeruginosa, Aeromonas hydrophila, Xanthomonas campenstris, Zooglea filipendula, Leuconostoc cremoris, Clostridium botulinum, Enterobacter aerogenes* and *Aerococcus viridians*.

The trend of microbial load corroborates with Okpokwasili et al. (2005) that observed that human pathogens in water decreases with increase in the days of degradation. The decrease in the microbial load of the wastewater is perhaps associated with organisms making use of the organic materials present in the water for their biological activities. According to Michael (2013), decrease in nitrogen and phosphorus levels as well as decrease in organic materials in water led to decrease in microbial load of organisms in that water. According to Willey et al. (2006), these organisms are found as normal flora of soil, water and certain foods and may therefore be found where foods are decaying. According to Nester et al. (2004), the presence of this organism often found in wastewater makes wastewater unsafe for animal consumption.

Physico-chemical and metal parameters of wastewater samples

There was an increase in the temperature of the domestic wastewater subjected to degradation (Figure 3 down right). At day 0, low temperature was recorded with the highest temperature in postgraduate hostel wastewater and the least temperature was observed in Resque hostel wastewater. An increase was also noted with days of degradation with the highest temperature on day (32), the highest temperature for day (32) was found in junior staff quarters wastewater (29.5°C), while the least temperature was recorded in Aba hostel wastewater (28.2°C).

The pH (Figure 3 down left) shows increase with days of degradation. At day 0, senior staff quarters and Akindeko hostel samples had the least and highest pH of 7.10 and 7.78, respectively while at day 32, values increased to 9.20 (postgraduate hostel wastewater). The total suspended solids results (Figure 3 top left) shows that the wastewaters were highly polluted on day 0 due to high value recorded. Reductions were observed with degradation days where the highest at day 32 was 7.15 mg/l from postgraduate hostel. From Figure 2 top left, there was slight decrease in dissolved oxygen (DO) of the wastewaters samples with degradation days, high values were recorded at day 0, during the course of degradation, there was slight reduction to day 32 with

Table 1. Biochemical characteristics and identification of bacterial isolates.

Sample	Gram stain	motility	Spore	Catalase	citrate	lactose	Fructose	mannitol	arabinose	Maltose	Probable organism
Ak1,Pg_1,Jq_1, An_1,Jb_1,Ab_3, Req_3,Abh_3,Sq_1	-	+	-	+	-	-	A	A	-	A	*Serratia mascensces*
Ak2,	-	+	-	+	-	A	-	-	A	-	*Streptococcus faecalis*
Ak3,An5, Sq3	+	+	+	+	-	-	-	A	A	A	*Staphylococcus aureus*
Ak4	-	-	-	+	-	-	A	-	-	-	*Shigella dysenteriae*
Ak5,Jb3,Abh2,Snq4	+	+	+	+	-	-	A	A	-	A	*Bacillus substilis*
Ak6	-	+	-	-	-	-	A	-	A	-	*Pseudomonas aeruginosa*
Ak7, Pg4, Jq2, An4, Sq2,Abh, Req4,Ab5,Jb2	-	+	-	+	-	-	A	A	-	A	*Proteus vulgaris*
Pg2	+	+	-	-	-	-	A	A	A	A	*Aeromonas hydrophila*
Pg3	+	-	-	-	-	-	-	-	-	A	*Zooglea filipendula*
An6,Ak8,Abh, Req5	-	+	-	+	-	+	A	A	A	A	*Escherichia coli*
Jb5	-	-	-	-	-	A	A	A	A	A	*Xanthomonas campenstris*
Ab1,Abh1	+	-	-	+	-	A	-	A	-	A	*Leuconostoc cremoris*
Ab2,Abh6											*Clostridium botulinum*
Abh6,Req2	-	-	-	+	+	A	A	A	-	A	*Klebsiella pneumoniae*
Ab6,Req1	-	+	-	+	+	A	A	A	A	-	*Enterobacter aerogenes*
Abh4,Snq5	+	+	-	-	-	-					*Aerococcus viridians*

+ = Present, - = absent, A = Acid production. Ak = Akindeko hall, Pg= postgraduate hall, Jq= Junior staff quarters, An= Annex hall, Wl= Wolef hostel, Jb= Jibowu hall, Req= Resque hall, Ab= Abiola hall, Abh= Aba hall, Sq= senior staff quarters.

postgraduate hostel wastewater having the highest value of 4.11 mg/l and Resque hostel wastewater had the least value of 1.67. The highest biochemical oxygen demand in Figure 2 down left was on day (0) with the value of 4.96 mg/l in Akindeko wastewater and the least value of 2.69 mg/l was recorded in Resque hostel wastewater. During degradation, there was reduction in the BOD with the highest on day 32 observed in Jibowu hostel wastewater (2.20 mg/l) and the least value of 0.44 mg/l was recorded in Resque wastewater. The conductivity of the wastewaters in Figure 2 top right increased with days of degradation with the highest conductivity recorded on day 32 with 763 mg/l and the least value of 318 mg/l was found in Annex hostel wastewater.

The total dissolved solid of the samples increased gradually with degradation in Figure 2 top left, the highest value was recorded on day 32 with the value of 813 mg/l in Annex hostel wastewater and the least value on the same day was 405 mg/l in Resque hostel wastewater. The mineral analysis (Figures 4 to 5) showed decreased values in all the samples with degradation days. The result of the physico-chemical properties of wastewater subjected to degradation showed that pH plays a major role on the rate of degradation. According to Adams and Moss (1999), degradation rate increases with

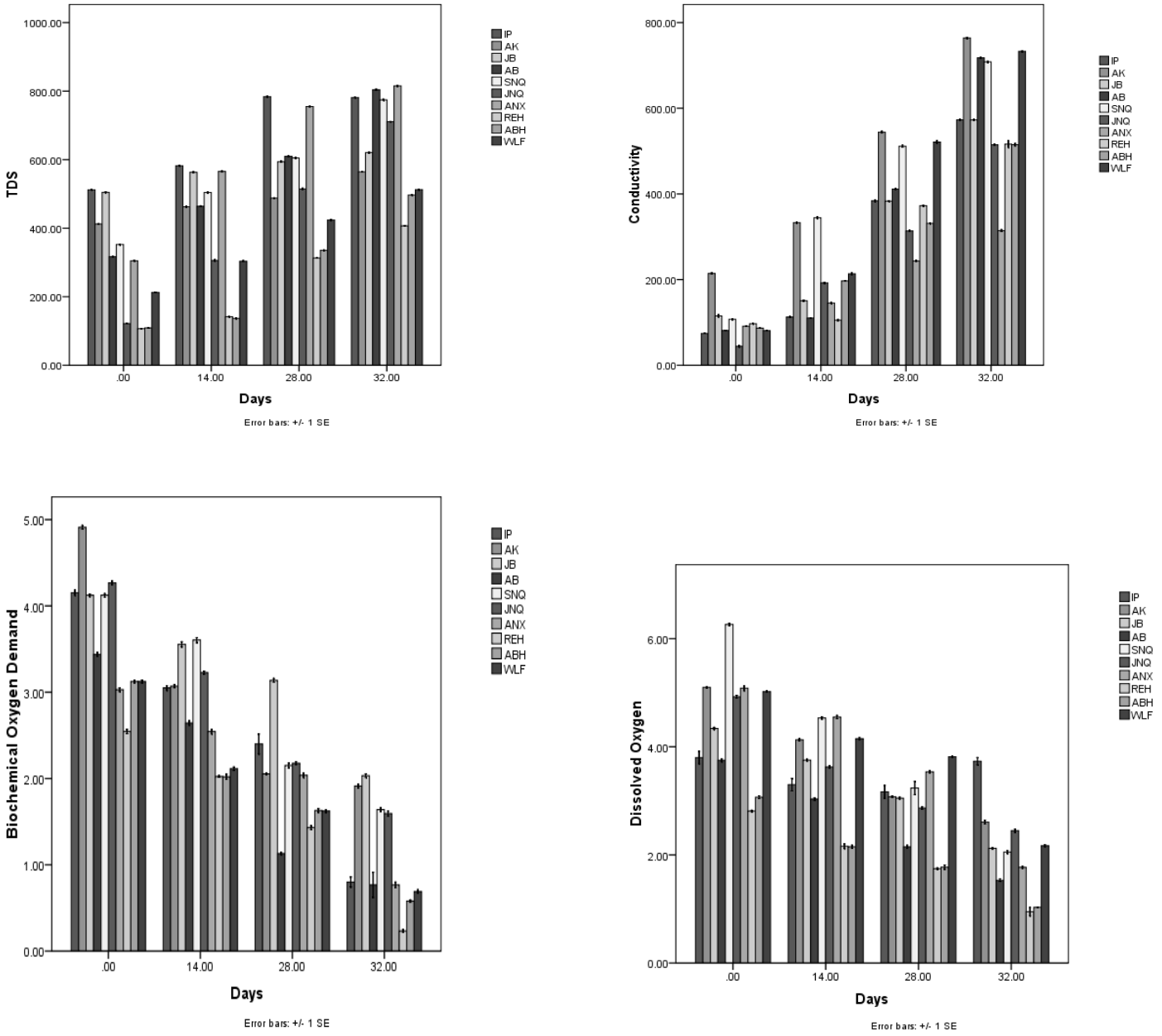

Figure 2. Total dissolved solids (mg/ml) (top left), conductivity (top right), biochemical oxygen demand (mg/ml) (down left) and dissolved oxygen (mg/ml) (down right) readings of wastewater samples.

increase in pH level of waste and wastewater. The results obtained in this work also corresponds to that of Willey et al. (2006) which stated that the rate of degradation increases with increase in pH. The increasein temperature is an indication that degrading activities is on the increase. According to Nester et al. (2004), increase in temperature of degrading liquid is usually due to microbial activities on the substrate and particles present in waste or fluid on which they feed. The total suspended solids in the wastewater showed that as degradation progresses, there is a reduction in the total suspended solids. This may be due to the fact that the microorganisms present in the wastewater may feed on these suspended solids for their survival. According to Robert et al. (2006), suspended solids which include food particles provide the bulk of food on which the

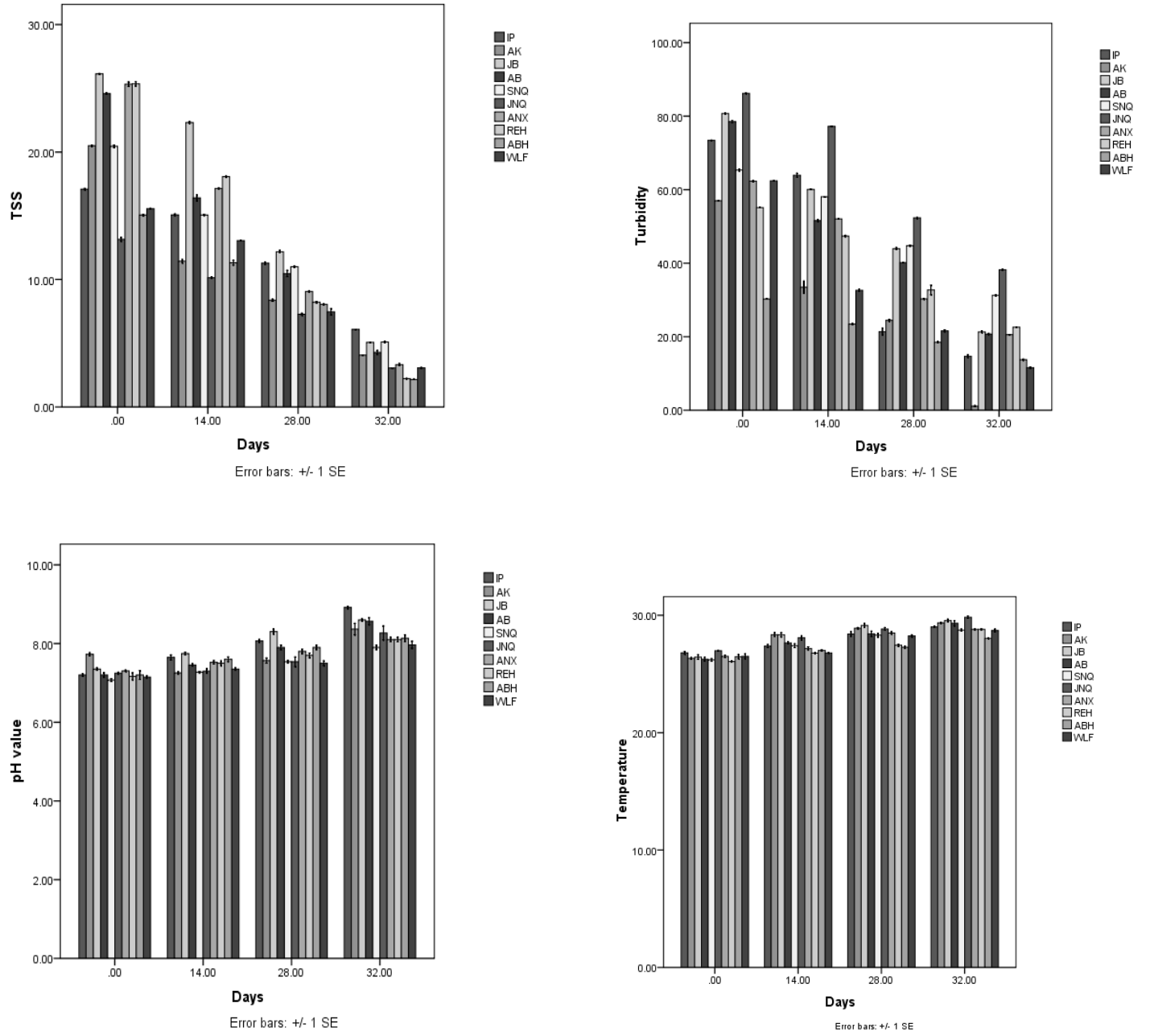

Figure 3. Total suspended solids (top left), turbidity (top right), pH value (down left) and temperature (down right) readings of wastewater samples.

microorganisms present in such water samples feed. Dissolved oxygen and biochemical oxygen demand both decreases respectively with increase rate of degradation. Oxygen in the wastewater would have been used up by the microorganisms degrading the wastes in the wastewater as the days increased. Okoh et al. (2007) obtained similar result in which the oxygen demand and biochemical oxygen demand reduced as degradation progressed. The wastewater conductivity on the other hand increased with increase in days of degradation. According to Wasserman et al. (2006), increased conductivity is as a result of breakdown of solid mineral particles that may be in the water. Also, Vilia-Elena (2006) reported that increased conductivity in water may be due to microbial activity on the solid waste particles being activity on the solid waste particles broken down

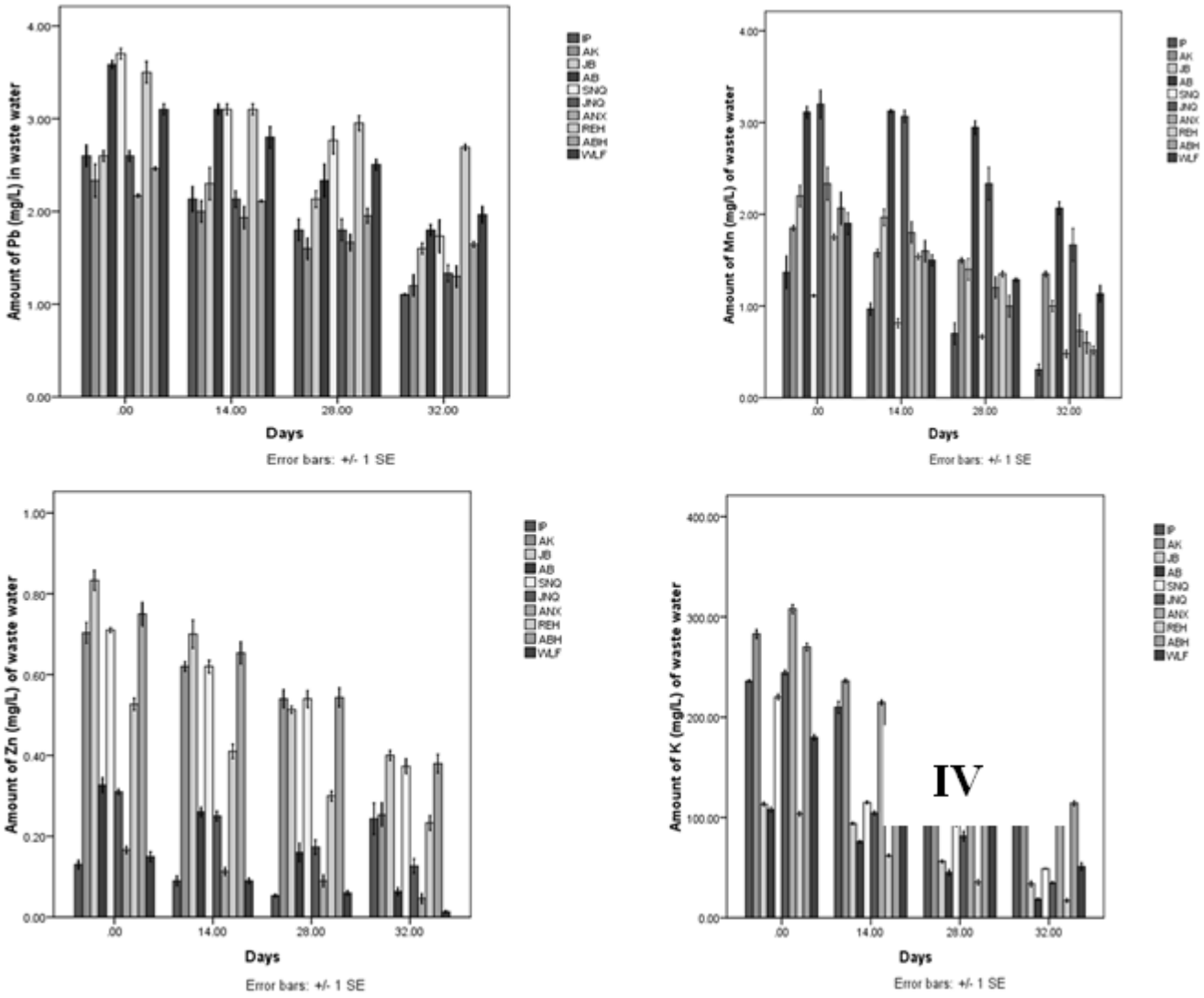

Figure 4. Amount (mg/L) of lead (top left), manganese (top right), zinc (down left) and potassium (down right) in domestic wastewater samples.

by the microorganisms present in such water. Therefore, increased conductivity in the result obtained could be due to either one of the two reasons or a combination of both reasons. Okoh et al. (2007) also reported the two reasons to be responsible for the increase in the total dissolved solid of wastewater. Therefore, increased total dissolved solid obtained in this work is in agreement with Okoh et al. (2007). Igbinosa and Okoh (2009) emphasized the utilization of major minerals in water by organisms for metabolic activities as being responsible for decrease in minerals during degradation of wastewater. This is also in agreement with the result obtained in this work. Degradation has significant effect on both microbial and physico-chemical parameters of wastewater; there is also obvious impact on the mineral analysis of wastewater.

Conclusion

Wastewater effluents are major contributors to a variety of water pollution problems. The discharge of these wastewaters into water bodies without proper treatment has impact on the water quality. Incorporation of low technology management practices such as primary settling should be carried out to reduce the period of delayed degradation. This study emphasizes the information that treatment of wastewater will reduce the microbial content of the wastewater hence mitigate

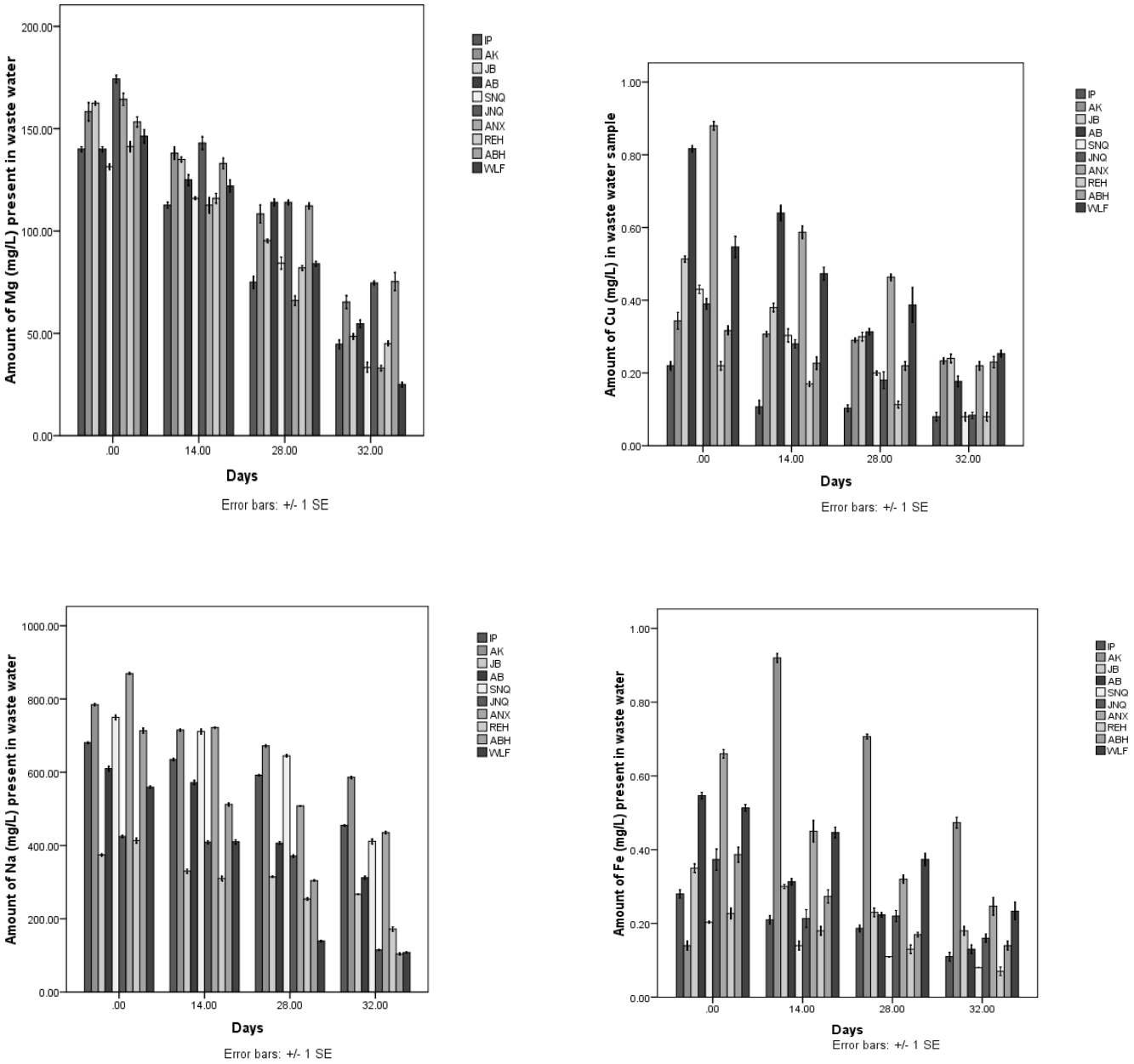

Figure 5. Amount (mg/L) of copper (top left), iron (top right), sodium (down left) and magnesium (down right) in domestic wastewater samples.

associated diseases from these microorganisms. The physico-chemical and mineral analysis before and after degradation are also an indication that these parameters can be altered to suite safety. To achieve unpolluted wastewater discharge into receiving water bodies, there is the need for careful planning, adequate and suitable treatment, regular monitoring and appropriate legislation. This will enhance science-based decisions and ensure the sustainability of the environment and the health of plants and animals.

Conflict of interests

The authors have not declared any conflict of interests.

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Pollution by endocrine disrupting estrogens in aquatic ecosystems in Morogoro urban and peri-urban areas in Tanzania

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This study aimed to assess the extent of pollution of aquatic ecosystems by endocrine disrupting estrogens particularly the ethinylestradiol (EE2), estrone (E2) and estradiol (E1). The study was carried out in Morogoro urban and peri-urban areas. The main sources of fresh water for domestic uses, fishing and agricultural activities in the study areas including the Mindu dam catchment area, Ngerengere and Morogoro Rivers were assessed. The endocrine disrupting estrogens in water samples were identified and quantified using competitive Enzyme Linked Immunosorbent Assay (ELISA) kits. The recovery of estrogens in this study ranged from 65 to 90.22%, the range which is within the acceptable level. The levels of estrogens in Ngerengere River ranged from non-detectable levels to 0.68, 0.03 to 8.42 and 0.05 to 16.97 ng/L for EE2, E2 and E1, respectively. At Mindu Dam the levels ranged from 0.07 to 0.3 ng/L, 0.41 to 2.1 ng/L and 2.6 to 6.5 ng/L for EE2, E2 and E1 respectively. Furthermore, for Morogoro River the levels ranged from undetected to 0.92, 0.34 to 9.53 and 0.17 to 11.49 ng/L for EE2, E2 and E1 respectively. Mean concentrations in control samples and those in upstream and midstream of the rivers were comparable ($p > 0.05$). But the mean concentrations in downstream portions were significantly higher than those in control samples ($p < 0.05$). These concentrations however, were below those reported in other studies to cause harmful health effects. Hence, the extent of pollution was not significant enough to cause adverse health effects to aquatic organisms and human.

Key words: Ethinylestradiol, estradiol, estrone, micro pollutants, Ngerengere River, Morogoro River.

INTRODUCTION

The aquatic ecosystems are the ultimate sink of most environmental pollutants originating from natural and anthropogenic sources such as industries, livestock farms, agricultural fields, hospital wastes, domestic wastes and municipal effluents. Several studies in Europe, Asia and USA have reported that sewage effluents are major contributors of manmade chemical pollution in rivers (Gomes et al., 2003; Mitani et al., 2005;

Huerta et al., 2016). On the other hand, runoff associated with waste from animal farming has been reported as another potential source of estrogens in the rivers (Williams et al., 2007; Kolok et al., 2007; Yuan et al., 2014; Huang et al., 2016).

Endocrine disrupting estrogens are among the emerging pollutants which end up in aquatic environment (Snyder et al., 2009). They are termed emerging because there are no established guidelines for environmental monitoring however, have adverse health effects to wildlife and human (Nosek et al., 2014). Estrogens are potent endocrine disruptors at concentrations frequently observed in surface water (Wedekind, 2014). They tend to bioaccumulation in aquatic organisms, such as algae which acts as scavenger or sinks for estrogens (Maes, 2011). In addition, food-web model predicted the bioaccumulation of estrogens in all organisms at low level (Lai et al., 2002).

Reproductive impairment have been reported in various species of fish in many countries due to exposure to estrogens (Jobling et al., 2003; Hinck et al., 2009; Ingram et al., 2011; Caldwell et al., 2012; Guellard and Soko, 2015; Huang et al., 2016). Both natural hormones (E1 and E2) and synthetic hormones (EE2) have endocrine disrupting effects such as reduced fertility and feminization of male fish (Tyler and Jobling, 2008; Bhandari et al., 2014; Iwanowicz et al., 2016). Exposure of male fish to estrogens can result in a range of effects from the complete sex reversal in most severe cases to different degrees of feminization including intersex and decreased expressions of secondary sex characteristics (Tabata et al., 2001; Gross-Sorokin et al., 2004; Lange et al., 2008; Länge et al., 2012).

Laboratory studies have shown that the estrogens have additive effects (Thorpe et al., 2003). Thus, even if the concentration of one of them is below the lowest observable effects, the combined effect can be significant. The EE2 is more potent in induction of reproductive abnormalities than the natural estrogens (Aris et al., 2014). It can induce vitellogenin formation in some male fish species at concentrations of as low as 1 ng/L and induce intersex of fish at 4 ng/L, whereas E2 can induce vitellogenin formation at 5 ng/L and induce intersex at 10 ng/L (Metcalfe et al., 2001; Thorpe et al., 2001).

The aquatic ecosystems in Morogoro Urban and Peri-urban areas include Mindu dam and its catchment, Ngerengere River, Morogoro River and other seasonal and permanent streams. Morogoro municipal effluents from wastewater stabilization ponds are discharged into Morogoro River, hence could be a potential source of estrogen pollution. In addition, within Morogoro urban there are several industries such as sisal, textile and leather. It has been observed that untreated or poorly treated effluents are being discharged into the Ngerengere and Morogoro rivers. Generally, the industrial development strategy in Tanzania was pursued without environmental regulation for a longtime and consequently many industries do not have waste treatment facilities (United Republic of Tanzania (URT), 2006). Furthermore, the land along the rivers and Mindu dam is used for agriculture, livestock breeding, residential, public and commercial purposes. Therefore, the ecosystems are prone to pollution from natural and anthropogenic sources.

Previous research in Morogoro aquatic ecosystems focused on pollution due to solid waste, nutrients, pesticides and heavy metals (Franks et al., 2005; Mdegela et al., 2009; Mero, 2011). On the other hand, another study dealt with interactive effects of mixed pollutants on biomarker responses in sewage wastewater and fresh water aquatic ecosystems in Morogoro (Mdegela et al., 2010). Generally, in Tanzania the research coverage on emerging pollutants such as endocrine disrupting estrogens are very limited (Miraji et al., 2016).

Despite the presence of endocrine disrupting estrogens in the environment, no guidelines have been established by Tanzania Bureau of Standards. The current guidelines TZS 860: 2005 with limits for municipal and industrial wastewaters includes chemical pollutants other than estrogens (TBS, 2005; EWURA, 2014). Furthermore, even World Health Organization (WHO), United Nations Environment Programme (UNEP), European countries United States Environmental Protection Agency (USA EPA) and Australian EPA are still collecting more research evidences so as to establish the guidelines for estrogens in the environment (WHO and UNEP, 2012). Therefore, it was necessary to carry out this study so as to establish a basis from which future researches on estrogens in Tanzania can rely on. In addition, the likely source and extent of pollution in aquatic ecosystem by endocrine disrupting estrogens needed to be assessed and mitigation measures be planned and implemented.

Description of the study area

Morogoro river originate from Uluguru mountains, it passes through Morogoro Urban eventually joins Ngerengere river between Kihonda and Tungi areas which are within Morogoro urban (Figure 1). There are

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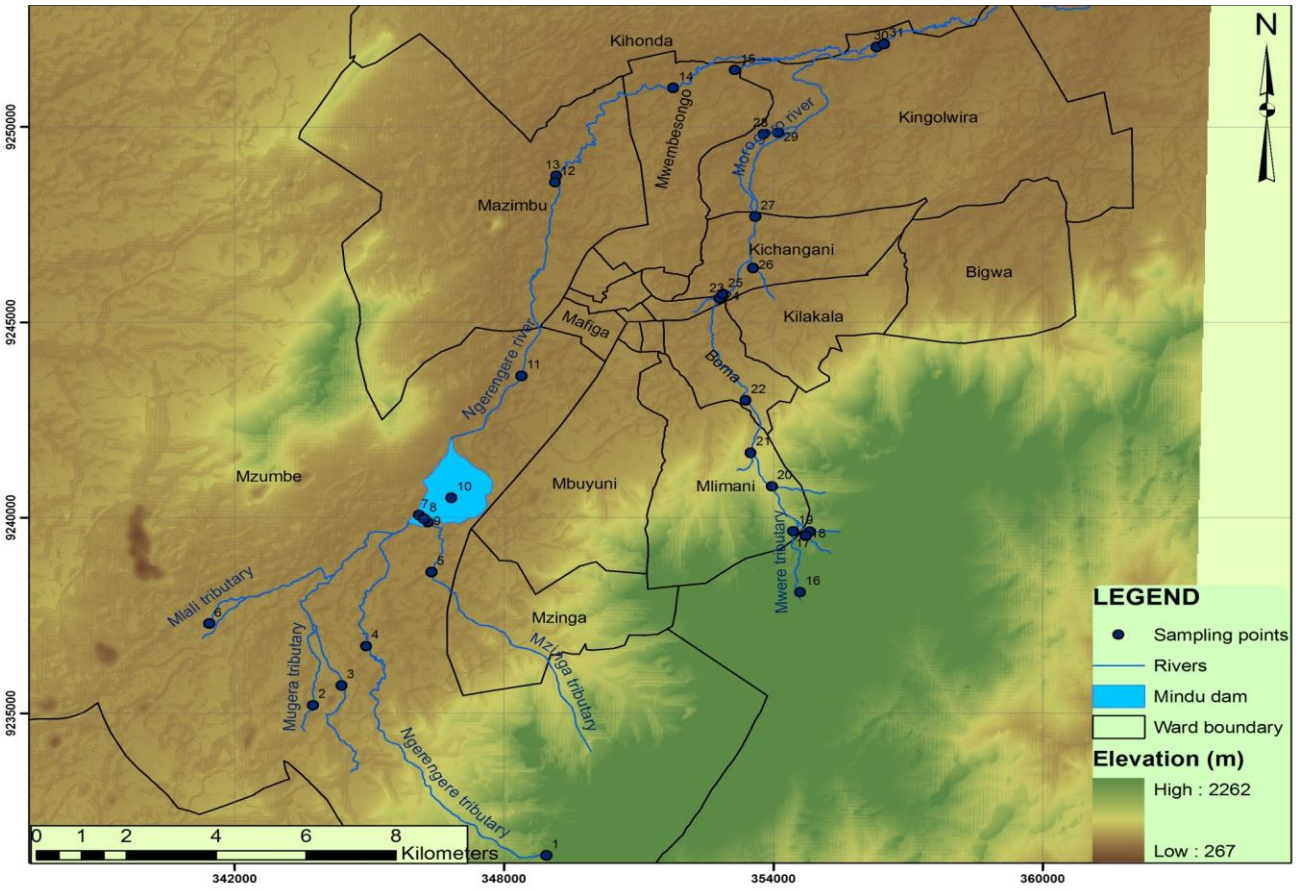

Figure 1. Map of Sampling Points in Aquatic Ecosystems in Morogoro Urban and Peri-urban areas.

seven tributaries which join Morogoro River. Those tributaries are Sole, Mwere, Kitundu, Mdirila, Mlali, Kikundi and Kilakala. Ngerengere River also originates from Uluguru Mountains, along with four other tributaries, namely Mzinga, Lukulunge, Mugera and Mlali. Water from these tributaries is collected in the Mindu dam whose purpose is to supply drinking water to Morogoro urban area but also used for fishing activities. From the Mindu dam, the river passes through Morogoro urban towards the east (Figure 1). It finally joins the lower Ruvu River which discharges its water into Indian Ocean after passing through Coast region. The Ruvu River is the main source of domestic water supply to Dar es salaam city.

MATERIALS AND METHODS

Chemicals and materials

Two standards ethinylestradiol (EE2) and β-estradiol (E2) hormones were supplied by Santa Cruz Biotechnology, Texas, USA. Other chemicals used were n-heptane (99%), methanol (99%), acetone (99.8%) and hydrochloric acid (37%, 1.18 M) supplied by Carlo Erba Reagenti and Sigma Aldrich, Germany. Glass fiber filter papers of MN 615, size Ø 150 mm and 2576 size; Ø 240 mm from Macherey-Nagel GmbH and Co.KG, Duren-Germany and Munktell and Filtrak GmbH, Barenstein Germany respectively, and solid phase extraction C-18 cartridges (130 mg, 3mL) by Varian and Chromabond.

Sampling of water samples

Purposive sampling strategy was adopted based on connections to perceived hotspots of estrogenic pollution. As described in Table 1, samples were drawn from each tributary which join Morogoro and Ngerengere rivers as well as from industrial wastewater and Municipal effluents getting into the rivers. Samples were also drawn from points of which the researchers hypothesized that pollution could be enhanced due to agricultural runoff as well as domestic wastes. Apart from those points also samples were drawn from point sources of the rivers where neither agricultural activities nor human settlement occurred. For Mindu dam, samples were drawn about 100 m from rivers entry points, three points were sampled and the fourth point was selected at mid of the dam.

Composite sampling being a technique that combines a number of discrete samples collected from a body of material into a single homogenized sample for the purpose of analysis (Australian, 2005) was adopted in this study. Composite sampling reduces costs of

Table 1. Description of the sampling sites in Morogoro Urban and Peri-urban Aquatic Ecosytems.

Aquatic ecosystem	Sampling sites clusters	sampling sites cluster description
Ngerengere River	Control site	Ahead of Mnyanza Village in Uluguru Mountains, around and beyond the site no human settlement and activities, just a forest, hence represent the river source with no significant pollution
	Before Mindu Dam (BM)	Included five sampling sites from separate tributaries namely, Mzinga, Lukulunge, Mugera, Mlali and Ngerengere tributary. All tributaries enter into Mindu Dam, in the areas around the sampling site there were moderate human settlement, agricultural activities and to a lesser extent livestock keeping
	Mindu Dam (M)	Collect water from five tributaries and other seasonal streams, fishing activities are carried out. The dam is reliable source of fresh water for Morogoro Urban. In Dam water samples were drawn from four sampling sites
	After Mindu Dam (AM)	Included two sampling sites, at Kasanga bridge and Mazimbu bridge,
	After Mazimbu Sewer (ASW)	Included two sampling sites, near Mazimbu Campus sewer pump were in some incidence raw sewage used to leak into the river and at Kihonda bridge before the river received effluent from industries
	After Industrial Effluent (AIND)	Included three sampling sites, a point about two hundred meters after the entry of industrial effluent, a point few meters after Morogoro River joining the Ngerengere River and industrial effluent before joining the river
Morogoro River	Control	Ahead of Morning Site centre, in Mugu Forest Reserve, around and beyond the site no human settlement and activities, just a forest, hence represent the river source with no significant pollution
	Upstream (UP)	Comprised six sampling sites from five tributaries namely, Sole, Mwere Kitundu, Mdirila and Mlali tributaries, as well as a point near Rock Garden hotel; around the tributaries there were very little agricultural activities and fewer human settlements.
	Midstream (Mid)	Comprised four sampling sites, namely, Kikundi and Kilakala tributaries, a point before Kikundi tributary entry, and at Fungafunga centre. Around the sites there were intensive human settlement, health centres, dispensaries, hotels, markets. Hence suspected to be more polluted than the upstream
	Downstream (DW)	Included three sampling sites, at Msamvu bridge, after entry of Mafisa WSPs effluent and After joining Ngerengere River. The sites suspected to be more polluted due the domestic waste, livestock waste, industrial waste as well as the municipal effluents

environmental and public health assessments, while maintaining and often increasing the precision of sample based inference (Patil, 2002). At each sampling point three samples each 500 ml were drawn and thoroughly mixed in glass bottle to make a 1.5 L of composite sample. In addition, composite tape water sample was drawn immediately after Morogoro Urban Water and Sewarage Authority fresh water treatment unit. The pH of water samples was adjusted to about 3 by adding hydrochloric acid so as to fix the estrogens. The added acid suppressed microbial activity which could degrade the estrogens to some extent before analysis (Havens et al., 2010). Thereafter, the samples were carried in cool box packed with ice packs to the Ecotoxicology and Natural Products research Laboratory in the Faculty of Veterinary Medicine at Sokoine University of Agriculture, for pretreatment and solid phase extraction of estrogens that was done within 12 h after sample collection.

Extraction of estrogens from water samples

Extraction of estrogens from water samples was carried out according to the protocol described by Hansen et al. (2011) with some modifications customized to our laboratory settings. Each water sample (1.5 L) was first filtered twice using GFC filters papers to ensure removal of debris. Solid phase extraction was performed with C18 cartridges (Bond Elut 500 mg, 3cc reservoir, Varian Agilent Technologies, USA) and vacuum manifold. The C-18 cartridges were conditioned with 2×3 mL heptane, 3 mL acetone, and lastly with 3 ml of distilled water. After extraction the cartridges were dried in air using vacuum manifold for about half an hour, and then eluted using a mixture of 10 ml of heptanes and acetone (65:35). The eluate was then air dried at 30°C, and then reconstituted in 5 ml methanol. The samples were stored at -20°C before being analysed by enzyme linked immunosorbent (ELISA) competitive technique. The ELISA technique was used because it is cost effective method and has detection limit which is lower than the existing methods for screening estrogenicity (Mauricio et al., 2006; Pool, 2008).

Detection and quantification of estrogens by ELISA competitive technique

The detection and quantification of EE2, E2 and E1 was carried out using ELISA kit from Cloud-Clone Corp. 1304 Langham Creek Dr. Suite 226, Houston, TX 77084, USA. Manufacturer instructions were followed; immediately measurement on microplate reader was conducted at 450 nm.

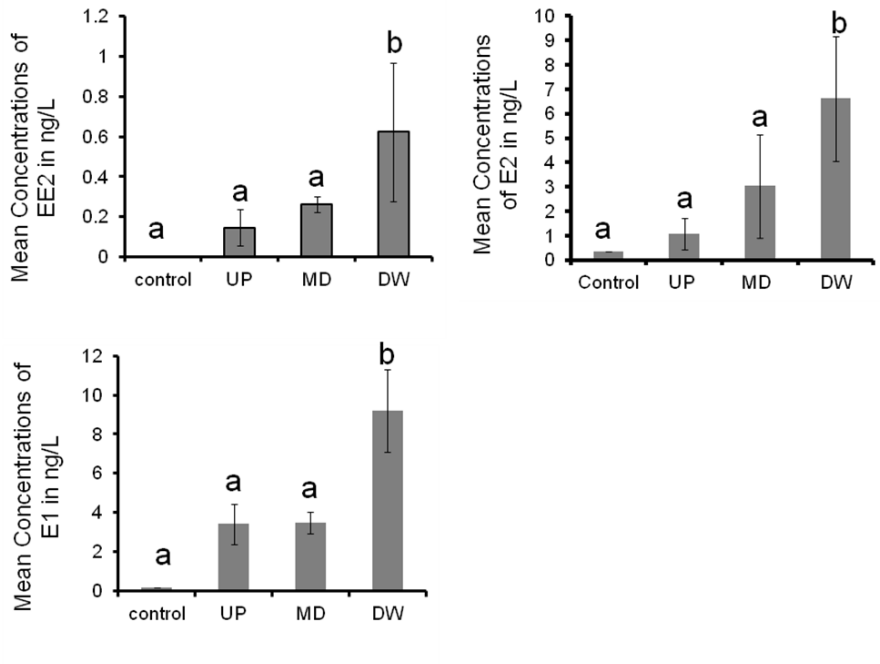

Figure 2. Mean concentrations of estrogens (EE2, E2 and E1) in sampling Sites clusters of Morogoro River. UP = upstream MD = midstream DW = down stream

Quantitative data analysis

The concentrations of the standards (2, 0.67, 0.22, 0.074 and 0.025 ng/ml) were transformed into natural logarithm to obtain linear calibration curve, in turn natural logarithm of concentration for each hormone was drawn against the respective absorbance. The linear equation obtained in the curve was used to interpolate the concentration of estrogens in samples.

Recovery studies

Four different concentrations (2, 1.33, 0.13 and 0.013 ng/ml) of mixture of standard EE2 and E2 each was made by dissolving in 1500 ml distilled water. The same pretreatment and analysis steps were followed as was done for water samples.

Statistical analysis

IBM SPSS version 20 was used for statistical analysis of the results; both descriptive and inferential statistics were carried out. For descriptive statistics means, standard deviation, median and range were calculated. Inferential statistics one way ANOVA with post hoc Tukey's-b was employed for multiple comparisons of estrogens levels between sampling site clusters. Level of significance between groups was reported at $p < 0.05$.

RESULTS AND DISCUSSION

Estrogens standard curves

Natural logarithms of standard concentrations were plotted against absorbance to obtain linear curves (Suppl Figure 1). The R2 for EE2, E2 and E1 was 0.9707, 0.9851 and 0.982 respectively. Hence, the linear equations were used to quantify the estrogens based on their respective absorbance.

Recovery results

The recovery of EE2 and E2 were assessed for solid phase extraction and ELISA technique analysis. The results are as shown in Suppl Table 1

Identified and quantified endocrine disrupting estrogens in water sample from Morogoro River

Figure 2 shows the mean concentrations of identified and quantified natural and synthetic endocrine disrupting estrogens from Morogoro River. The results indicate that there were no significant difference in levels in upstream and midstream for all three estrogens ($p \geq 0.05$). However, the downstream levels were significantly higher ($p < 0.05$) than those at midstream and upstream sampling points. The midstream and upstream levels were comparable ($p \geq 0.05$) to those found in control samples. Hence, the extent of pollution at upstream and midstream was low. At control site only natural estrogens (E2 and E1) were identified and quantified but at very low

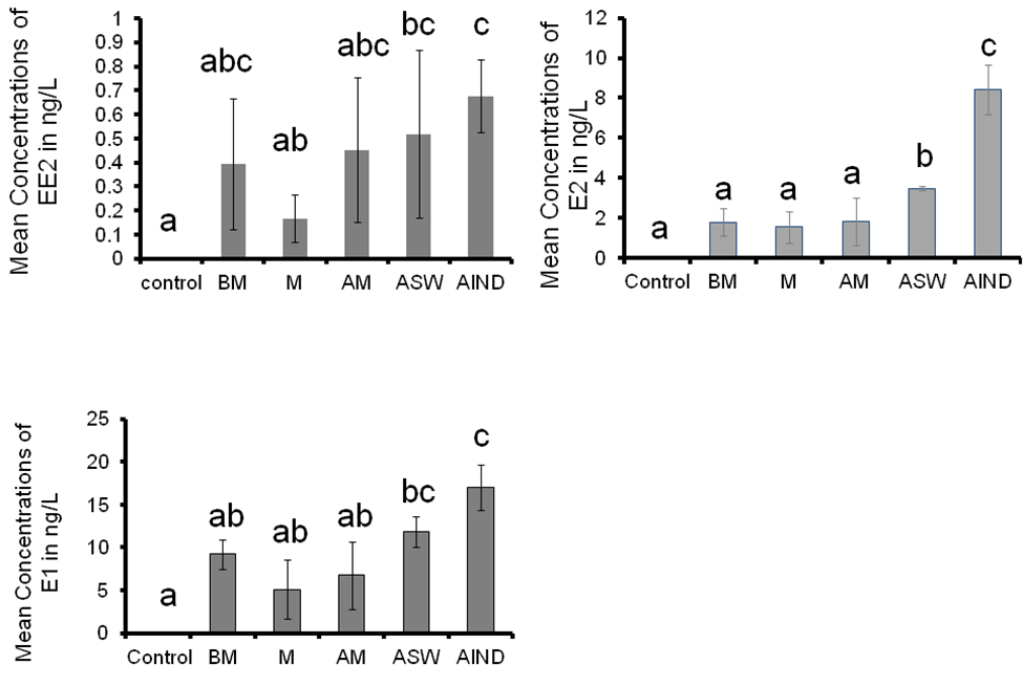

Figure 3. Mean concentrations of estrogens (EE2, E2 and E1) in sampling sites clusters of Ngerengere River water samples.
BM = Before Mindu dam, M = Mindu dam, AM = After Mindu dam, ASW = After Mazimbu Sewer, AIND = After Industrial Effluent.

concentrations where E1 was found to be 0.17 ng/L and E2 was 0.34 ng/L. This implied that, those natural estrogens could be from animals dwelling in the forest. No traces of ethinylestradiol could be identified, therefore the results concur with the actual field situation in which no human settlement and activities were found. In upstream the levels of E1, E2 and EE2 ranged from 2.08 to 4.7, 0.48 to 2.17 and 0.019 to 0.22 ng/L, respectively. Whereas, in midstream ranged from 2.7 to 4.09, 1.13 to 4.91 and 0.21 to 0.3 ng/L for E1, E2 and EE2, respectively. Although the levels in midstream sites were relatively higher than those found at upstream, the difference was insignificant ($p < 0.05$). The midstream sites were prone to more pollution owing to the intense human settlement and activities. For instance, a site named before Kikundi tributary ranged highest for all three estrogens due to pollution from domestic effluent, effluent from the bus terminal, as well as effluent leaking from hospitals. Essentially, low standard of sanitation and sewage in all of Tanzania's urban centres including Morogoro urban attributed to pollution (URT, 2006). In downstream sites, levels ranged from 7.37 to 11.49, 5.67 to 9.5 and 0.24 to 0.92 ng/L for E1, E2 and EE2 respectively. These sites received Morogoro Municipal effluent from wastewater stabilization ponds at Mafisa, also industrial effluent as well as waste from livestock farming. For instance, at Kichangani cattle farms were found near the river, hence could contribute to pollution of the river by estrogens. This observation is supported by finding reported by Williams et al. (2007), Kolok et al. (2007), Yuan et al. (2014) AND Huang et al. (2016), Animal farms are potential sources of natural and synthetic estrogens. In addition, several studies reported that WSPs are potential sources of estrogens pollution in rivers (Mitani et al., 2005; Gomes et al., 2003; Sim et al., 2011; Belhaj et al., 2014). The main source of EE2 in rivers could be the use of contraceptive by residents in domestic/commercial houses (Lei et al., 2009; Laurenson et al., 2014). In all samples the levels of EE2 were the lowest of all three estrogens, indicate that the extent of pollution by domestic waste was low or proportion of women who were using contraceptive pills in the study area was low.

Identified and quantified endocrine disrupting estrogens in water sample from Ngerengere River

Figure 3 displays the mean concentrations of identified and quantified natural and synthetic endocrine disrupting

Table 2. Endocrine disrupting estrogens concentration range in Ngerengere River sampling sites clusters.

Clusters of sampling sites	Endocrine disrupting estrogens concentration range (ng/L)		
	E1	E2	EE2
BM	6.52 - 10.15	1.06 - 1.99	0.17 - 0.84
M	2.58 - 6.52	0.41 - 2.1	0.07 - 0.3
AM	5.68 - 7.89	0.03 - 4.04	0.51 -0.8
ASW	10.69 - 13.12	3.47 - 3.5	0.27 - 0.77
AIND	15.09 - 18.84	7.5 - 9.3	0.57 - 0.78

estrogens in Ngerengere River. There were no significant difference between the control site samples and those collected Before Mindu (BM) and within Mindu dam sites for all of the three estrogens ($p \geq 0.05$). In addition, mean concentrations for estradiol in samples collected After Mindu (AM) had no significant difference with the control samples. The results implied low extent of pollution, hence low health risks to aquatic organisms and human. However, considering levels at specific sites some had levels which could be enough to induce reproductive abnormalities in aquatic organisms. For instance samples from Mlali tributary contained 0.84 and 11.26 ng/L for EE2 and E1, respectively. The tributary received domestic effluent leaking from Changarawe Village. The Figure 3 shows that “After Industrial Effluent” (AIND) sampling cluster had significant higher mean concentration of the estrogens compared to other clusters. This observation is attributed by effluent from industries, Morogoro River which join Ngerengere River after receiving effluent from Morogoro Municipal WSPs as well as accumulation of domestic effluent and livestock waste. For estrone “After Mazimbu Sewer” (ASW) sampling cluster had significant higher level than other clusters except AIND which had statistically similar level to ASW. Table 2 displays the estrogens concentration range in Ngerengere River sampling sites clusters. The highest concentration of EE2, E2 and E1 were 0.84, 9.3 and 18.84 ng/L, respectively. The results imply low extent of pollution.

The results in this study show a similar trend to those reported by Kinoshita et al. (2010). It was observed that significant contamination of Thailand and Malaysia rivers with estrogens occurred in urban areas, contrary to remote areas where no detectable level was observed. Apart from that, the levels of estrogens in this study were lower than those reported by Lei et al. (2009), in which Dagu River, in China E1 ranged from 5 to 55.3 ng/L, E2 ranged 0.93 to 33.4 ng/L and EE2 ranged from not detected to 35.6. For Yongding New River in China ranged from 0.64 to 20.2 ng/L for E1, from non-detected to 13.6 ng/L for E2 and from non-detected to 12 ng/L for EE2. The third river named Beitang River in China E1 ranged from 4.29 to 49.8 ng/L, for E2 from 2.51 to 21.2 ng/L and EE2 was from 1.64 to 24.4 ng/L. In addition, Rao et al. (2013) reported that estrogens from three river water samples in Tianjin, China ranged from 0.64 to 50, 1.87 to 11.5 and 1.55 to 24.4 ng/L for E1, E2 and EE2 respectively. Furthermore, Rocha et al. (2016) reported an unexpectedly high level of estrogens in Mira River in Portuguese, obtained an annual average estrogen 57 ng/L.

Health implications

Estrogens even at low concentrations in the environment can have harmful effects on aquatic organisms and in humans, who might be consuming water or food contaminated with estrogens (Gustavo et al., 2014; Gross-Sorokin et al., 2004). Feminization or demasculinisations of molluscs, arthropods and fish have been reported in polluted lakes or rivers (Guillette et al., 2007; Krein et al., 2012). Effects shown in wildlife or experimental animals may also occur in humans if they are exposed to EDCs at a vulnerable time and at concentrations leading to alterations of endocrine regulation (UNEP and WHO, 2012; Bhandari et al., 2014). Concentrations which led to vitellogenin induction have been reported in previous studies as low as 5 ng/L for estradiol (Tabata et al., 2001), 3.2 ng/L for estrone and around 1 ng/L for ethinylestradiol (Fenske et al., 2001; Thorpe et al., 2001). The intersex condition has been recorded in various fish species following exposures to concentrations as low as 10 ng/L each for estradiol and estrone (Metcalfe et al., 2001; Tabata et al., 2001) and 4 ng/L for ethinylestradiol (Länge et al., 2001). Furthermore, Caldwell et al. (2012) reported that fish exposure to 17 beta-estradiol at concentration that exceeds 10 ng/L cause intersex in some species of male fish.

Based on previous other published studies on concentration of estrogens which lead to observable health defects to aquatic organisms, the concentration of estrogens obtained in this study have low health risks to aquatic organisms and humans. However, long-term exposure of aquatic organisms to such low concentrations

can lead to significant health risks due to bioaccumulation (Lai et al., 2002). Therefore, measures should be taken to minimize pollution of the water bodies by endocrine disrupting estrogens.

Conclusion

The most potent estrogens namely ethinylestradiol, estrone and estradiol were identified and quantifies in aquatic ecosystems in Morogoro Urban and Peri-urbans areas. The results implied lower extent of pollution in the aquatic ecosystems by endocrine disrupting estrogens. However, a few sampling sites had significant higher concentration of estrogens, but dilution offset the impact. The sources of pollution mainly were industrial effluents, effluent from livestock farms, residential wastes, and effluents from wastewater stabilization ponds. Ethinylestradiol (EE2) which is the most potent estrogen, its concentrations was the lowest of all three estrogens in all samples. In addition, the EE2 concentrations were below (< 1 ng/L) to those reported in other studies that could bring observable health defects to aquatic organisms. Furthermore, the concentrations of estradiol and estrone in most samples could not cause observable health defects except in some sampling sites, could induce vitellogenin formation in male fish. No detectable estrogens were found in tape water. Therefore, the extent of pollution has low health risks to aquatic organisms and humans.

Conflict of Interests

The authors have not declared any conflict of interests.

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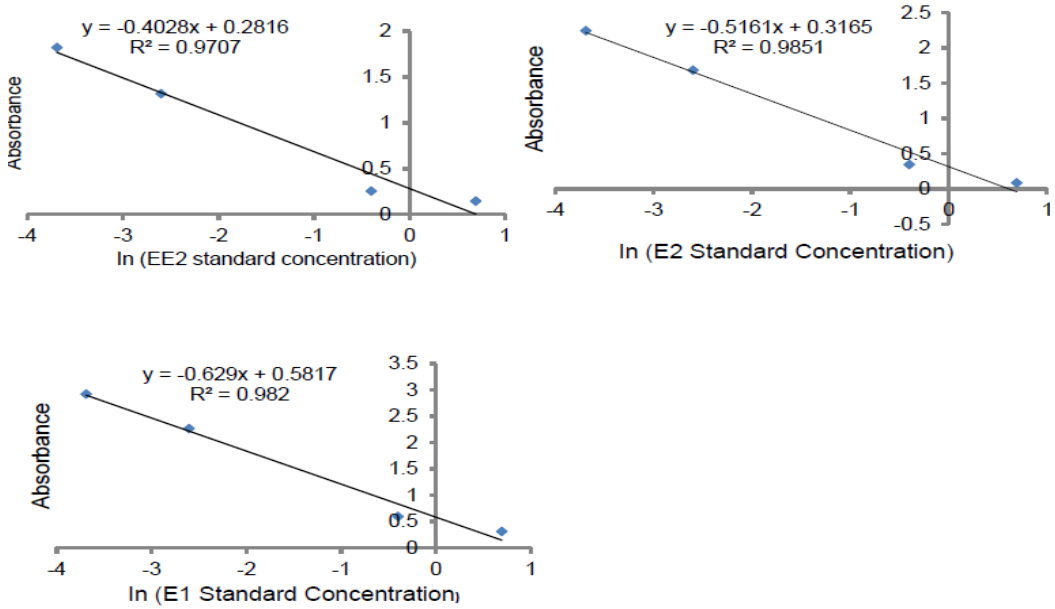
Suppl Table 1. Percent Recovery for E2 and EE2.

Concentration of EE2 and E2 spiked in distilled water ng/ml	Recovered concentration EE2 ng/ml	%Recovery EE2	Recovered concentration E2 ng/ml	% Recovery E2
2	1.34	67	1.30	65
1.3	0.98	75.4	0.89	68.5
0.133	0.112	84.21	0.12	90.22
0.05	0.043	86	0.045	90



Suppl Figure 1. Calibration Curves for EE2, E2 and E1.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