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Dr. Surender N. Gupta  
Faculty, Regional Health and Family Welfare Training Centre, Chheb, Kangra-Himachal Pradesh, India. Pin-176001. Area of Expertise: Epidemiologist
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Biodegradation of pyrene by a mixed culture isolated from hydrocarbon-polluted soil

Baba Shehu Umar Ibn Abubakar¹*, Norhafizah Abdullah², Azni Idris², Mohamad Pauzi Zakaria³ and Mohd Yunus Shokur⁴

¹Department of Civil and Water Resources Engineering, Faculty of Engineering, University of Maiduguri, P. M. B. 1069, Maiduguri, Borno State, Nigeria.  
²Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Malaysia.  
³Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 UPM Serdang, Malaysia.  
⁴Department of Biochemistry, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 UPM Serdang, Malaysia.  

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This paper presents the biodegradation of pyrene (C₁₆H₁₀), a four-benzene-ring polycyclic aromatic hydrocarbon (PAHs) using a mixed culture of bacteria. The mixed culture was enriched from hydrocarbon-polluted soil sample, using a plate incubated with a thin film of pyrene. The isolates were identified biochemically as Bacillus cereus and Enterobacter aerogenes. The mixed culture bacteria degraded approximately 90% of the pyrene in aqueous medium within six days of incubation. The assessment of other environmental factors necessary for the activity of the mixed culture revealed that the mixed culture grows well between pH of 5.0-7.0 and temperatures of between 20-30°C. From the results of this trial therefore, it is suggested that the mixed culture has good potential for bioremediation applications.

Key words: Pyrene, biodegradation, mixed culture, polycyclic aromatic hydrocarbon (PAHs), environmental factors.

INTRODUCTION

Pyrene (Pyr) is a polycyclic aromatic hydrocarbon (PAHs) containing four benzene rings fused together (C₁₆H₁₀) with a molecular weight of 202 g/mol. It has relatively lower vapor pressure and higher partition coefficient than other low molecular weight PAHs, poorly soluble in aqueous solutions, but is easily volatilized into the atmosphere. It is known as an unwanted by-product of gasification and other incomplete combustion processes (Juhasz and Naidu, 2000; Mrozik et al., 2003). However, its aromatic structure contributes to its high chemical stability, as is also the case in the localization of electrons between adjacent conjugate bonds in high molecular...
weight PAHs (Schwurzenbach and Gschwend, 2003). The persistence of Pyr in the environment is attributed to its chemical stability, low water solubility and high absorption capacity to soil matrix; as a result, it is low biodegradable (Yan et al., 2004). Although not as carcinogenic as benzo[a]pyrene (BaP), it has nonetheless, been reported among other carcinogenic PAH molecules. Pyr could impair the skin or other sensory organs and has a long-lasting effect on terrestrial and marine organisms (Peng et al., 2008). Consequently, Pyr is listed among the priority environmental pollutants by the United States Environmental Protection Agency (US EPA) (Yan et al., 2004).

Microbial degradation is among the numerous factors that determine the fate of Pyr in the environment. Although recalcitrant, some studies have confirmed the ability of microbes to degrade Pyr: Bacillus species (Samanta et al., 2002), Burkholderia species (Deng et al., 2012), Cycloclasticus species (Samanta et al., 2002), Mycobacterium species PYR-1, Mycobacterium flavescentis (Ho et al., 2000), and Sphingomonas species (Daugulis and McCracken, 2003). These pure cultures of bacteria usually have difficulties of survival especially when introduced to contaminated sites, due to stiff competition and the lack of adaptability leading to poor survival in the newly introduced environment (Goldstein et al., 1985). This is particularly important when considering in-situ remediation of soils contaminated with PAHs.

Even though variety of pure bacterial isolates can degrade Pyr in the laboratory culture, inoculating pure culture to the environment for bioremediation purposes still remains a great challenge and may not be feasible, because of the aforementioned inoculum limitations. Previously, studies have used bacteria in the form of mixed consortium (Luo et al., 2009; Yu et al., 2005), as well as an indigenous form isolated directly from soil (Goldstein et al., 1985) that are capable of degrading PAHs. Presumably, the use of mixed cultures as a solution may be worth evaluating: to utilize a synergistic approach in degrading the recalcitrant compound. During mineralization, a parent compound may be transformed through different series of metabolic process by members of the mixed culture and has been reported that the first metabolic product of biodegradation could be a carbon source for another strain within the culture consortium (Luan et al., 2006). In the process, the parent compound could be biodegraded to its benign stage. Consequently, the application of a mixed culture or consortium of bacteria may be a more effective alternative to the use of pure cultures. The objective of this work was to isolate a mixed culture of bacteria degrading Pyr from used-oil-dump-soil from a local automobile workshop. This was because petroleum contaminated soils or sediments harbor varieties of hydrocarbon-degrading microorganisms; therefore, isolating a mixed culture with diversity of metabolic capabilities would be used to solve the inability of pure culture in remediating contaminated sites.

**MATERIALS AND METHODS**

**Chemicals**

Chemicals such as Pyr 98% purity, analytical reagent standard of methanol, acetone, dichloromethane and acetonitrile are of high performance liquid chromatography (HPLC) standard purchased from Fisher Scientific Inc. (Malaysia). Other PAHs such as napthalene (Nap) with 99% purity, phenanthrene (Phn) with 97% purity and flouranthenene (Fla) with 98% purity were purchased from Fisher Scientific Inc. (Malaysia). All the glass wares, flasks, test tubes, sample bottles used in this study were washed with detergent, sonicated and washed three times with methanol, acetone and hexane in succession in ensuring removal of any organic contaminant that could interfere with the experiments. Because organic chemical such as PAHs tend to stick to the glass body and thereby interfere with the quality of the work, stock solutions for PAHs were prepared in acetone solvent.

**Collection of soil samples**

A polluted soil sample was obtained at a dumping site of an automobile workshop (near Bangi, Selangor, Malaysia). The site has been used for over fifteen years and made up of a one-side-opened drum where all oil and grease washed out, used crankcase oil and condensed engine oil were dumped. The drum was filled and overflowed on the surrounding soils causing the soil beneath to be highly contaminated with hydrocarbons. These soils were chosen as a potential source for indigenous microorganisms with hydrocarbon tolerant. A sample of soil smelling with hydrocarbon was scooped with hand trowel and poured carefully into a zip-lock bag, placed in a cooler and transported to the laboratory prior enrichment and isolation steps.

**Preparation of culture media**

Chemicals of analytical grade purchased from Fisher Scientific (Malaysia) were used in the media preparation. A mineral salt medium (MSM), which was used for culture media has the following compositions and this formulation is according to Tao et al. (2007). 5.0 mL of phosphate buffer solution per litre, containing: 566.5 × 10⁻⁵ mM K₂HPO₄, 312.5 × 10⁻³ mM KH₂PO₄, 466.5 × 10⁻³ mM NaH₂PO₄·12 H₂O, 471.5 × 10⁻³ mM NH₄Cl; mineral salts solution (561 × 10⁻³ mM MgSO₄, 1.539 × 10⁻³ mM FeCl₃, 327.9 × 10⁻³ mM CaCl₂); trace elements solution (236.1 × 10⁻³ mM MnSO₄, 265.18 × 10⁻³ mM ZnSO₄ and 28.08 × 10⁻³ mM (NH₄)₂MoO₄·2H₂O). This (MSM) was used throughout this work.

**Enrichment and isolation of Pyr degraders**

A sterile nutrient broth (NB, 100 mL) was prepared in 250-mL conical flask with 2 g of the polluted soil sample added into it followed by incubation at 180 rpm and 30°C for 24 h in order to harvest enough Pyr-degraders. Thereafter, 2 mL of the 24 h old growth culture was inoculated aseptically into a 100-mL mineral salt medium (MSM) and Pyr (15 ppm) dissolved in acetone was poured into the flask. The sample was incubated at 30°C with 180 rpm agitation for 2 weeks. Further, 1 mL of culture was transferred to
MSM media supplemented with 15 ppm Pyr for further enrichment step. This step was repeated until the culture is considered acclimatized with Pyr. This culture was used as a stock culture for Pyr degradation and subsequent isolation step. Isolation of Pyr-degraders was performed by streaking plate method. Briefly, several MSM-agar plates supplemented with Pyr were prepared and streaked. Colony showing a clear zone on MSM agar supplemented with Pyr was scored as positive, subsequently picked and repeatedly streaked several times and finally stored using enriched nutrient agar medium.

**Preparation of mixed culture inoculum**

Several isolated strains were individually incubated using a NB media supplemented with 0.15 ppm of Pyr at 30°C under 180 rpm agitation in the dark. After reaching the late exponential phase using optical density (OD) at 600 nm (OD_{600}=0.8-0.9), the cells were harvested by centrifugation at 3500 rpm for 20 min. Then, the cells were resuspended in 50 mL MSM medium and remixed until the suspension was homogeneous. From each culture, 100 μL was added to a mixed culture of fourteen different isolates. This mixed culture was stored with 20% glycerol and kept at -80°C until further use.

**Determination of cell concentration**

All the glassware including flask, measuring cylinders and pipettes were washed thoroughly and dried in an oven at 60°C for 24 h. All the glasswares were autoclaved at 121°C for 15 min in an Autoclave SX-700, Tokyo, Japan. A mineral salt medium (MSM) supplemented with 1000 ppm of yeast extract was prepared and autoclaved (121°C for 15 min). A 500-mL conical flask was filled with 400 mL of (MSM+yeast extract) and the pH adjusted to 7.2 using 2 M phosphate buffer. Thereafter, 1 mL inoculum was introduced into the 500-mL flask containing 400 mL MSM-yeast extract. The flask was then incubated in an orbital shaker at 30°C (at 180 rpm agitation) for 24 h.

After 24 h, the culture was divided into an equal volume of 200 mL each. The first portion was centrifuged at 6000 g at 5°C for 5 min. Then the supernatant was removed, and the cell pellet dried for 24 h at 65°C to achieve a constant cell dry weight. From the other remaining 200 mL portion, 1 mL of sample was measured for turbidity with distilled water as diluent (where necessary) and measured at 600 nm. Series of dilution were plotted against turbidity/absorption at 600 nm. A correlation curve was obtained using the cells dry weight of the mixed microbial culture. This procedure was conducted according to Alfermann et al. (1994).

**Identification of Pyr-degraders**

All the samples were identified biochemically in the Department of Bacteriology, Faculty of Veterinary Medicine, Universiti Putra Malaysia. The Pyr-degrading consortium was routinely cultured on Pyr-supplemented MSM liquid medium as earlier described and was inoculated into growth tubes containing the standard diagnostic substance and reactants listed in Table 1. In addition, the cells were Gram stained. The consortium grew well on Pyr-supplemented MSM medium in the laboratory, and after extensively subculturing, maintained their growth rate and Pyr-degrading activity (Quinn et al., 1994).

**Biodegradation study on Pyr**

The inoculum was developed using a stock culture of enriched mixed bacterial consortium by growing in a sterilized MSM medium containing 1.5 ppm Pyr for a week, or until the growth reaches late lag phase. 1 mL of inoculum was further subcultured into 100 mL of MSM at pH 7.2 with an initial concentration of 1.5 ppm and 3.0 ppm of Pyr respectively. A flask without any bacterial inoculum was also prepared with 1.5 ppm of Pyr as the control for abiotic loss during degradation studies. Then, an inoculum size of 1% (v/v) was inoculated aseptically into culture flasks. The cultures were incubated in an oven shaker (180 rpm agitation) at 30°C in the dark. The growth and Pyr degradation were monitored over a period of 12 days by taking triplicate flasks of each concentration and abiotic samples every 24 h. The aqueous samples were monitored with a spectrophotometer (HACH, DR/2500) at 600 nm and converted to cell dry weight using the correlation curve as previously described. The biomass growth in the aqueous samples was quantified and reported in microgram per litre dry weight. Other PAHs compounds: Naphthalene (Nap), Phenanthrene (Phn) and Floranthene (Fla) were also tested with the mixed culture using the same technique. The residual of Pyr and other PAHs tested were quantified using HPLC method described in “Extraction and Analysis Pyr”. Biodegradation percent in all the experiments were calculated according to Equation 1:

\[
\text{Biodeg} = \left(\frac{\text{Pyr}_{\text{res}} - \text{Pyr}_{\text{fls}}}{\text{Pyr}_{\text{res}}}\right) \times 100
\]

Where Biodeg= % degradation, \(\text{Pyr}_{\text{res}}\) is residual Pyr concentration in the control, \(\text{Pyr}_{\text{fls}}\) is residual Pyr concentration in degradation flask. To meet quality assurance and quality control (QA/QC) on Pyr determination, all the analytical procedures were checked by a known concentration of surrogate internal standard m-typhenyl. Recovery of Pyr was back-calculated using the surrogate. Also, a blank experiment was performed on every batch of sample analysed. In case of GC-MS, auto-tuning was done every time of sample injection.

**Extraction and analysis of Pyr**

1 mL of aqueous sample was extracted with dichloromethane three times in equal volume. Aqueous sample was filtered with pre-dried anhydrous sodium sulphate (dried at 200°C for 2 h) through a funnel lined with glass-wool bed filter. The filtrate was collected and subjected to concentration step using a rotary evaporator at reduced pressure and concentrated to 1 ml under slow nitrogen purging. The quantification of Pyr was conducted using a high-performance liquid chromatograph (Shimadzu HPLC, Japan) equipped with UV detector. Phenomenex Synergi 4 m Max-RP80A column (250 × 4.6 mm) was used with a water-acetonitrile mobile phase in a gradient mode at a fixed flow rate of 1.5 mL/min. The column was equilibrated with 35% acetonitrile in distilled water for 2 min and its concentration was increased linearly at rate of 2.7% per minute to 100% in 24 min, and then held up for another 10 min. The temperature of column was set at ambient condition, and column eluent was detected at 254 nm. The unknown samples were quantified using standard Pyr calibration curves. However, other PAHs (Nap, Phn and Fla) were quantified using separate correlation curves developed with DCM as carrier solvent and detected with a spectrophotometer.

**Identification of metabolite of Pyr**

Sample from the culture medium between the lag phase and exponential phase were submitted to Analytical Laboratory, Department of Chemistry, Faculty of Science, Universiti Putra Malaysia. The samples were analyzed using GC (GC-17A Ver.3)
Table 1. Biochemical characteristics of Pyrene-degrading pure isolates.

<table>
<thead>
<tr>
<th>Test</th>
<th>Group 1 (12 samples)</th>
<th>Group 2 (2 samples)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth at room temperature 37°C</td>
<td>Aerobic</td>
<td>Aerobic</td>
</tr>
<tr>
<td>Description of colony</td>
<td>Greenish large rod</td>
<td>Grayish large rod</td>
</tr>
<tr>
<td>Gram stain</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Hemolysis</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Catalase</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Blood broth</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Trehalose Lactus</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>SIM (sulphide/indole mobility)</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Glucose</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Sorbitol/Sucrose</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Dextrose nitrate reduction</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Urea</td>
<td>NA</td>
<td>-</td>
</tr>
<tr>
<td>TSI</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

Group 1 = *B. cereus*; Group 2: *E. aerogenes*.

RESULTS

Biochemical characteristics and identification of PAH-degraders

A soil sample taken from aged petroleum dumping site was used as a potential re-source for PAH-degraders. Strains were enriched and acclimatized to Pyr condition for approximately two months, and selected colonies with Pyr-degrading potential were biochemically characterized and identified. It was a common practice to use higher concentration for enrichment stage. For example, Yu et al. (2005) and Tam et al. (2003) used 10 ppm of PAH. In this study, 15 ppm Pyr was adopted as a primary instigation on a condition of no alternative carbon source other than Pyr as a strategy to encourage fast acclimatization of the selected consortium. All the isolated strains were characterized as aerobic bacteria and grew well at a temperature of 37°C. 12 Gram-positive with code numbers of WT10 (1) and WT10 (2) appeared as a grayish large rod. They grew rapidly within 24 h of incubation at 37°C except for the two Gram-negative strains, which were grouped as slow growing degraders.

To encourage the growth of slow growing bacteria, the media was supplemented with 0.75 ppm of Pyr during inoculum preparation; also, Pyr may encourage the slow growing ones to grow together with fast growing degraders. All the 12 Gram-positives indicated relatively positive reaction to almost all the biochemical test such as: hemolysis, catalase, blood broth, trehalose/lactose, SIM (sulphide/indole mobility) glucose, sorbitol/sucrose, dextrose nitrite reduction, urea, oxidase and triple sugar iron agar (TSL). In contrast, the 2 Gram-negative reacted only with citrate. The 12 Gram-positive and the 2 Gram-negative isolates were identified as *Bacillus cereus* and *Enterobacter aerogenes* respectively according to Jang et al. (1988).

Effect of environmental factors on degradation of Pyr

The ability of this mixed culture to grow well under different temperatures indicates that their growth and degradation of Pyr were affected by temperature changes after series of Pyr degradation test under different incubation temperatures of 20, 30 and 40°C, and at varying pH of 5, 6.5, 7 and 8. At incubation temperature of 20°C, the percent degradation of Pyr was the highest at pH 7 (92%) and the lowest was at pH 8 (37%). However, the percent degradation was about 85% at pH 6.5 under the same incubation temperature of 20°C as shown in Figure 1.

In contrast, at 30°C incubation temperature, there was
highest percent degradation of Pyr at both pH of 6.5 and 7, which was over 92% respectively, while at pH 5, the percent degradation was about 78% with the lowest percent degradation of 9% at pH 8 (Figure 1). The effect of temperature on percent degradation of Pyr was more pronounced when the incubation temperature was 40°C for all the pH range tested. The percent degradation was 34% at pH 7 but below 20% at either pH 5, 6.5 or 8 (Figure 1).

The result of the effect of pH on the percent degradation of Pyr at different incubation temperatures show that at pH 5, the percent degradation of Pyr were 92, 78 and 9% at 20, 30 and 40°C, respectively, whereas at pH of 6.5, the percent degradation of Pyr were 88, 98 and 37% at a temperature of 20, 30 and 40°C, respectively. Conversely, the percent degradations of Pyr at pH 7 were 95, 95 and 37% at 20, 30 and 40°C, respectively. The lowest percent degradations were recorded at pH of 8, with 37, 8 and 38% for 20, 30 and 40°C respectively (Figure 1).

Figure 2 shows the effect of pH on the concentration of biomass which indicated that at pH 4 there was long lag phase at about 3 days; and the biomass growth which was about 50 μg/mL as well as the growth which reached its stationary phase and lasted up to 3 days, subsequently dropped. At pH 5, the effect on the biomass growth equally shows long lag phase, but with a relatively higher biomass concentration of 78 μg/mL than pH 4. On the other hand, the effect of pH 6 on biomass production includes the growth having shorter lag phase than either pH 4 or 5, whereas the log phase started on 3rd day and reached its maximum on the 6th day. The biomass concentration of 60 μg/mL was obtained and was found to be less than that at pH 5; however, its biomass began to drop on the 8th day and continued till below 45 μg/mL on the 10th day. In contrast, biomass growth at pH 7 has a very short lag phase of 24 h only. It reached its highest biomass concentration on the 4th day of about 100 μg/mL, which was higher than all other pH range tested. pH 7 was the best for biomass growth having shorter lag phase and higher total biomass at the end of log phase (Figure 2). Since microbial groups have different pH preferences, drop or increase in pH beyond preference level may disrupt the plasma membrane or inhibit the activities of enzyme and membrane transport proteins. Therefore, a neutral pH of 7 might be preferential of this mixed culture; hence, it favors the higher growth rate and subsequently reducing the period of acclimatization.

However, it is significantly reduced to approximately similar values as other pHs on the 10th day (prolonged generation), a situation where bacterial cell uses a strategy to grow under a limited substrate concentration (Bren et al., 2013). This form of the growth strategy is very different from normal growth, where substrate concentration and nutrient supply were not limited. At pH of 8, there was a very long lag phase than all other pH. Its maximum biomass growth was reached on the 9th day and reduced on the 10th day. The highest biomass concentration at this pH was 60 μg/mL. Biomass concentration at alkaline pH of 8 was inferior to acidic; however, acidic condition at pH 5 is also considerable. This is also corroborated by estimated maximum specific growth rate μ_max obtained for all the pHs (Table 2).

pH 7 has highest specific growth rate (0.147 and 0.144 (h⁻¹)) at 1.5 and 3.0 ppm, respectively, and shortest lag phase (2 and 3 days) than the other pH tested. pH 4 and pH 8 both have lowest maximum specific growth rates (0.044 and 0.047 (h⁻¹)) respectively, however, pH 8 has the longest lag phase (8 days). External pH of 4 or below may lead to acid shock protein, prevent the denaturation of proteins and thereby retard the growth of the mixed culture. This may be the possible reason at pH 4 where the mixed culture growth rate was very low (0.044 (h⁻¹)) (Willey, 2008).
Biodegradation of Pyr

The mixed culture was tested on Pyr degradation in an aqueous medium containing MSM with Pyr concentration of 1.5 and 3.0 ppm as a sole carbon source. The growth was measured by OD at 600 nm and converted to dry weight using correlation curve in Figure 3, with $r^2$ of 0.989 which has been described by Alfermann et al. (1994) with little modification (using different carbon source) from the one reported by Alfermann et al. (1994).

The biomass growth and Pyr degradation occurred within six days of incubation. The lag period was very short indicating faster acclimatization and followed by a log phase from Day 2 to 6 with specific growth rate, $\mu$ at 0.147 and 0.144 h$^{-1}$, respectively (Figure 4).

Also, at 3.0 ppm there is better biomass growth while 1.5 ppm resulted in shorter lag phase, probably due to low concentration and assimilated easily, but with lower biomass harvest. Perhaps, the lower the concentration the lower the growth of biomass. Meanwhile, more than 80% of Pyr was degraded during this log phase growth period and can thus be classified as growth associated-degradation kinetics, indicating the overall growth of the mixed culture could be due to substrate consumption. This means that substrate consumption and degradation of Pyr followed a Monod-type growth pattern, which indicates that the mixed culture grew due to the consumption of Pyr as a source of carbon and energy. The growth curve and the percent degradation rate are given in Figures 4 and 5, respectively.

From Figure 5, there is a marked relationship with the rate at which Pyr was degraded by the mixed culture. The concentrations of Pyr dropped sharply at the initial stage in the 1.5 ppm concentration than from the 3.0 ppm. However, both concentrations were linearly reduced by 80% on the sixth day. In contrast, the degradation in the 3.0 ppm at 6 and 8 days slowed down but reached nearly 90% on the 10th day. From Figure 6, the abiotic control dropped from 1.5 ppm to 1.348 ppm and remained constant, accounting for about 10.1% loss. This could be attributed to volatilization or sticking to the wall of the glass.

**Utilisation of Pyr-degraders on other PAHs**

Other PAHs such as Nap, Phn and Fla were tested using the previous experimental setup as described earlier.
under “Methodology”. These PAHs were incubated as sole source carbon with the concentration of Nap, Phn and Fla of 0.86, 1 and 1.38 ppm respectively. They were incubated at 50 mL of MSM with pH 7.0, at 30°C, and 180 rpm in the dark and samples were taken at the end of two weeks. The result of degradation experiments for other PAHs, Nap, Phn and Fla (as source of carbon) in Figure 7 indicates that more than 90% of the three compounds were degraded within three weeks of incubation. In fact, the degradation of Fla is about 98%, and maybe because Fla is also a four-ring PAHs like Pyr, or the mixed culture may have metabolic capacity to degrade Fla. But, for the remaining two (Nap and Phn), they are LMW and are not recalcitrant to bacterial degradation, therefore easily degraded by the mixed culture. It has been proposed by Tam et al. (2003) that PAH-degrading bacteria enriched with any particular PAH compound as sole source carbon and energy could have the ability to metabolize varieties of alternative PAHs. The utilization of another PHA by a mixed culture has been reported (Yu et al., 2005; Yuan et al., 2000).

**Metabolites of Pyr**

To possibly identify any metabolite, a degradation culture...
sample was extracted using DCM three times. The sample was dried using anhydrous sodium sulphate and the extracts recombined and concentrated as previously described under “Methodology”. These samples were taken to the Chemistry Department, Universiti Putra Malaysia for GC-MS analysis. The results were interpreted based on the library similarity index provided by the software. Table 3 show some of the probable metabolites from the culture sample as revealed by the GC-MS chromatograph. There are many metabolites on Day 6, and benzoic acid, which is also one of the catabolic product of PAH degradation appeared on Day 4, 6, 8 and 10. Di-n-octyl phthalate appeared on Day 0, 2, 4 and 10.

**DISCUSSION**

The ability of *B. cereus* to transform Pyr into cis-4,5-dihydrodiol-4,5 dihydroxyppyrene in a single culture have been reported (Kazunga and Aitken, 2000); also, *E. aerogenes* in degrading Pyr has been reported in other works (Bastiaens, et al., 2000). The dominant member of the mixed culture is *B. cereus* from the soil exposed to hydrocarbon pollution. The enrichment was approached with a pure Pyr of about 98% purity as a carbon source.
solely. Therefore, the bacteria isolated were not as a result of other organic sources since the media used was mineral salt medium only. Although, from the isolation process, few members of *E. aerogenes* were isolated, it could be concluded that this strain prefers particular metabolite to the parent compounds. Despite the unavailability of experiments in this study to prove this, physical observations indicated that *B. cereus* colonies appeared first on agar plate during plate counting. The reason is that, at the early stage of incubation in an aqueous medium, only *B. cereus* were seen on the agar plates. Not until after six days before the *E. aerogenes* would begin to appear on the plates during plate counting for monitoring growth. Especially, during monitoring of growth in soil slurry batch reactor, colonies of *E. aerogenes* appear only on the six days.

For successful bioremediation of any organic contaminant, sufficient information on the microorganisms capable of mineralizing or degrading the contaminant to a benign and non-toxic end product is necessary. Several studies have been carried out on the isolation of bacteria, fungi, and algae that degrade varieties of aromatic hydrocarbons and other organic contaminants in the environment. Microbial isolation is done using the same method of enrichment and PAHs as the source of carbon and energy. For example, a polluted soil sample is serially diluted and plated on minimal basal salt (MBS) incorporated in agar, together with PAHs, or minimal salt medium (MSM) incorporated in agar and PAHs spread on the surface of the agar plate and incubated at certain temperature. This method was used by Kiyohara and Nagao (1978) for isolating bacteria degrading

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**Table 3. Probable metabolites of Pyr degradation.**

<table>
<thead>
<tr>
<th>No</th>
<th>RT GC</th>
<th>MW</th>
<th>Probable metabolites</th>
<th>Time Pyr Degrades (day)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.43</td>
<td>156</td>
<td>1,8-Dimethylnaphthalene</td>
<td>0 - 2 4 6 8 10</td>
<td>Cerniglia (1993)</td>
</tr>
<tr>
<td>2</td>
<td>9.65</td>
<td>204</td>
<td>Benzenepropanal</td>
<td>- - - + - -</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9.78</td>
<td>314</td>
<td>1,4-Benzenediolic</td>
<td>- - - + - -</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10.30</td>
<td>194</td>
<td>Benzoic acid</td>
<td>- - + + + + -</td>
<td>Kanaly and Harayama (2000)</td>
</tr>
<tr>
<td>5</td>
<td>10.80</td>
<td>184</td>
<td>2(3H)-Furanone</td>
<td>- - - + - -</td>
<td>Zeng et al. (2000)</td>
</tr>
<tr>
<td>6</td>
<td>10.45</td>
<td>178</td>
<td>Ethanone</td>
<td>- - - + - -</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>13.25</td>
<td>278</td>
<td>Dibutyl phthalate</td>
<td>- - - + - -</td>
<td>Peng Hua et al. (2012)</td>
</tr>
<tr>
<td>8</td>
<td>15.52</td>
<td>390</td>
<td>Di-n-octyl phthalate</td>
<td>- + + - - + -</td>
<td>Zeng et al. (2000)</td>
</tr>
<tr>
<td>9</td>
<td>3.82</td>
<td>156</td>
<td>1,2-Dioxane</td>
<td>- - - + - - -</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>7.43</td>
<td>198</td>
<td>6-Octen-1-ol</td>
<td>- - - + - - -</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>8.43</td>
<td>154</td>
<td>1,6-Octadien-3-ol</td>
<td>- - - + - - -</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>11.25</td>
<td>215</td>
<td>2-(phenilmethylene)</td>
<td>- - - + - - -</td>
<td>(Zeng Hong et al. (2000))</td>
</tr>
</tbody>
</table>

**Figure 7.** Percentage degradation of naphthalene, phenanthrene and fluoranthene at a concentrations of 0.86, 1 and 1.38 ppm, respectively. Each data point represents the mean of two replicates.
phenanthrene through identification of the clear zones surrounding the bacterial colony of interest. Heitkamp and Cerniglia (1989) also applied this method with little modification, using composite sediment and water samples exposed to radio-labeled [4-14C]Pyr and non-labeled Pyr. The Pyr-degrading bacteria were recognized as colonies surrounded by clear zones due to Pyr utilization. Due to these successes, many workers have applied this method either directly or with little modification; including Laehy et al. (2003), Yu et al. (2005) and Zhang et al. (2009) for PAHs isolation. In another method, PAHs crystals in liquid medium were also degraded with several subcultures in a fresh medium, as demonstrated by Bastiaens et al. (2000) and bacteria were isolated from sediment samples. Gaskin and Bentham (2005) compared the ability of different enrichment methods to select diverse, abundant bacteria population from contaminated soil samples; although, they found out that using Pyr alone as a source of carbon has lower ability to select diverse isolates; nonetheless, this study confirmed the suitability of Pyr as a carbon source.

Generally, to conduct biodegradation Pyr at 40°C was inferior compared to either 20 or 30°C; and is similar to the effect of temperature reported by Kim et al. (2005) and Kim and Freeman (2005). Temperature usually affects microbial degradation of hydrocarbon metabolism, and there is an optimum temperature beyond which biological activities often decreases (Riser-Roberts, 1998). In this study, therefore, the optimum temperature for the highest percent degradation of Pyr is between 20 and 30°C. Also, this result suggests that mixed culture could endure different temperature ranges from 20 to 30°C and thus have potentials for bioremediation application. Nevertheless, normal microbial metabolism would be usually affected by either too low or too high a temperature, thereby affecting the degradation of Pyr. Consequently, a temperature of 30°C was adopted for degrading Pyr in this study. This optimal growth condition was also reported by Zhang et al. (2009).

The ability of some bacteria to grow well under acidifying and neutral condition was also reported in the past by Wong et al. (2002). Biodegradation is also pH influenced; the percent degradation was highest around neutral (pH 6.5 - 7.0) and neutral pH was found to be the most ideal. This optimal pH and temperature values has been previously reported by Zhang et al. (2009) on biodegradation of PAH by bacteria. Temperature and pH are two important environmental factors that could determine the suitability of the environmental conditions to metabolic functions.

The hydrocarbon-polluted soil or sediment has been associated with diversities of pollutant-degraders with the ability to remove or degrade many recalcitrant organic contaminants (Yu et al., 2005). In a comprehensive bacterial diversity study of PAH-contaminated sites, Mueller et al. (1997) pointed out that PAH degradation capabilities of bacteria might not be unconnected with phylogenetic related genera; and are not restricted to a particular location. They stressed that uncontaminated aquatic sites might naturally harbor bacteria that can degrade PAH. However, it is challenging to obtain PAH-degrading organisms from uncontaminated soil sites. Several works reported that isolation of bacteria capable of degrading PAH could be easily obtained from the hydrocarbon-contaminated soil than otherwise (Tam and Wong, 2008; Tian et al., 2008). In this study, 14 Pyr-degrading bacterial strains were isolated from the hydrocarbon polluted soils, belonging to the genera of B. cereus and E. aerogenes.

Several reports indicated the suitability of a mixed culture than single strains. This is primarily due to their synergic response and better performance when compared to single pure culture (Mikesková et al., 2012). In the employment of defined mixed culture or co-culture of fungi and bacteria, synergic degradation capacity as compared to single strength was observed. Because of the synergic interaction among members or between members, one strain may attack the parent compound, or another may use the first metabolite as a carbon source (González et al., 2011). Although individual strength in a mixed culture has not been fully understood, detection of different strains in hydrocarbon polluted soils indicates individual strength in the transformation process (Ghazali et al., 2004).

It has been proposed by Tam et al. (2003) that PAH-degrading bacteria enriched with any particular PAH compound as sole source of carbon and energy could have the ability to metabolize varieties of alternative PAHs. The utilization of another PAH by a mixed culture has been reported by Yu et al. (2005). Apparently, some of the metabolites like Di-n-octyl phthalate were reported as metabolic product of initial ring fission of benzo[a]pyrene whereas others are from combined ozonation and bacterial degradation of Pyr (Zeng et al., 2000). Another aspect of this result is that some of the metabolites had higher molecular mass than Pyr, and were adjudged to be surfactants produced during degradation. This is so because, from physical observation of the culture medium during incubation as from Day 4 to 6, there were bobbles and thin films covering the surface of the medium. This could be due to productions of some surfactant; therefore, the mixed culture could have transformed some of the metabolites into some sort of surfactants to enable them dissolve the Pyr. The assumption is that Pyr has been completely degraded by the mixed culture; although there are differences between these metabolites and those reported due to pure culture. For example, Seo et al. (2010) found some metabolites that are similar to one found in this study.

Conclusion

Therefore, in this study, a mixed culture of B. cereus and
E. aerogenes was successfully enriched from a hydrocarbon- polluted soil using Pyr as sole source carbon and energy. The mixed culture degraded Pyr within a very short period as environmental factors such as pH and temperature affect the metabolic function of a microorganism. The result indicated that the culture performs well under a range of pH between 5-7 and a temperature range of 20 – 30°C. This isolated mixed culture could be a potential inoculum to ex-situ bioremediation of PAHs contaminated soils.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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REFERENCES


Full Length Research Paper

An assessment of total petroleum hydrocarbon and trace metal concentration in the sediments of Ugbo water way, South western Nigeria

Ashiru O. R.1,2*, and Ogundare M. O.1,3

1Department of Marine Science and Technology, Federal University of Technology, Akure, Ondo State, Nigeria.
2Institute of Deep-sea Science and Engineering, Chinese Academy of Sciences, Sanya, China.
3Department of Earth Sciences, Stellenbosch University, South Africa.

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Sediment samples from Ugbo water way, South Western Nigeria were assessed for total petroleum hydrocarbon (TPH) and trace metal concentrations. Seven sampling stations were selected and one control station. Total petroleum hydrocarbon (TPH) in the sediment samples was determined using Gas Chromatography-Flame Ionisation Detector (GC-FID) while trace metal concentrations were determined with Atomic Absorption Spectrophotometer (AAS). In situ measurement of the physicochemical parameters of the water was done during sampling. The average concentration of TPH in the sediment samples is 0.131 mg/kg which is far well below the maximum permissible limit (10 mg/kg) and the occurrence of the measured trace metals is in the decreasing order for the different metals Fe>Pb>Zn>Cu>Ni>Mn>Cd. Fe had the highest concentration with an average value of 0.845 mg/kg while Cd had the lowest average concentration of 0.032 mg/kg. The highest concentration of the TPH occurs at the point of offload of petroleum motor spirit (K5) and increases outwards in the down current direction as we travel away from K5. The levels of Cd, Fe, and Mn all exceeded the U.S.E.P.A recommended limit, while the rest of the metals (Pb, Zn, Cu, and Ni) were found to be within recommended limits.

Key words: Trace metal, pollution, physico-chemical parameters, sediment.

INTRODUCTION

Total petroleum hydrocarbon (TPH) is a mixture of chemicals which are made mainly from hydrogen and carbon, and so referred to as hydrocarbons. Some of the chemical components of TPH include hexane, jet fuels, mineral oils, benzene, toluene, xylene, naphthalene, fluorine, as well as other petroleum products and gasoline components. The concentration of TPH found in a study sample is indicative of the TPH contamination at that site and shows only little about how the particular petroleum hydrocarbons in the sample may affect people, animals,
and plants (U.S. DHHS, 1999). Petroleum hydrocarbons are ubiquitous contaminants and their residues persist in the environment, therefore they represent human health hazards (Wakeham, 1996; Lipiatou and Saliot, 1991). Macaulay et al. (Macaulay and Rees, 2014) stated that fundamental variation exists in the pathway for the dissipation of Total Petroleum Hydrocarbon (TPH) when spilled on land and water. Oil spilled on the sea surface undergoes various weathering processes simultaneously, such as spreading – influenced by wind, turbulence and the presence of ice on the water surface, evaporation, emulsification, photo-oxidation, dispersion, sinking, resurfacing, tar ball formation, and biodegradation – which makes oil spill control very difficult. Hence, the extent of the damage caused by the spill and the ease of clean-up depends on how quickly the clean-up response takes effect. The kinetics of these processes depends largely on sea conditions and the meteorological environment.

Trace metals occur naturally in the aquatic system from crustal materials through erosion but their concentrations in water may be increased through disposal of high metal waste and domestic sewage discharge. The occurrence of trace metals in water and biota therefore indicates the presence of natural and anthropogenic sources (Mahipal et al., 2016). This situation has led to many environmental agencies having regular monitoring exercises for monitoring their concentrations which is often compared against a standard of permissible limit. Trace metals are a serious pollutant in our natural environment because of their toxicity, persistence in the environment and bioaccumulation (Pekey et al., 2004).

Trace metals accumulate in sediments, in which they may not produce considerable ecological risk in the watershed but may be remobilized during biogeochemical processes, into the water column through water-exchange reactions such as re-suspension, desorption reactions and redox reactions, consequently enhancing the elevation of the dissolved concentration to a toxic level for aquatic biota (Vukosa et al., 2014; Yan et al., 2017).

This study investigates the suitability of surface water in Ugbo, Ilaje local government area (LGA) for domestic use and support of aquatic life. During the course of field related activities in the Ugbo environs, it was observed that the jetty is used for offloading premium motor spirit (PMS) into barges for onward transfer to the riverine communities in the area. A sheen along the water surface was observed, which may be as a result of the premium motor spirit spills in the course of discharge, with unusual brown coloration of the water (owing to the existence of dump sites, latrine and bathroom stalls along this waterway), and, brown oily films rimming any object that comes in contact with the water; spurred the authors to investigate the level of contamination along the Ugbo waterway particularly for Total petroleum hydrocarbon and trace metals. Sediment samples were collected for the purpose because in aquatic systems, sediments are generally known to be sunk for petroleum hydrocarbons, trace metals and other pollutants (Horowit, 1991).

There have been several typical researches on surface water monitoring and assessment in the country but these studies vary in methodology and purpose; as follows.

Ajao et al. (1996) worked on a review of pollution in coastal waters in Nigeria. They listed the various water bodies draining the country and grouped them based on the geology of their surrounding coasts (geomorphic units) (Ibe, 1988). They listed some of the sources of pollution in coastal waters including mining effluents, industrial effluents, domestic effluents and urban storm water runoff, shipping activities, Agricultural/ farmland run-off etc., and organic wastes. Other studies (Aderinola et al., 2009) included surface water, sediments and tissue of biological organisms from Lagos lagoon for trace metal concentrations. Sediments recorded higher concentrations values than water. Shellfish also showed a higher tendency for bioaccumulation than finned fishes.

Wogu and Okaka (2011) analyzed surface water samples from Warri, Delta State for nine trace metals including Cr, Cd, and V. They reported that Cd, Cr, Mn, and Ni had higher concentrations than standard Federal Environmental protection Agency (FEPA) limits for potable water, hinting at possible risks to public health. Taiwo et al. (2012) reported that industrial effluents make up the chief constituents of surface water pollution in Nigeria with industries releasing untreated water to the environment. They added that activities in the Niger Delta such as bunkering, oil theft, and pipeline vandalism have also been a major contributor to surface water pollution in that area. They concluded that variations in the quality of surface water experienced in the country reflects differences in land management and the physical environment, and surface water in urban areas are more prone to industrial effluents than rural areas.

Etim and Adie (2012) also reported on seven selected major rivers in southwestern Nigeria that Pb levels were beyond (WHO) limits for drinking water. And they found metal pollution index order was Pb>Cu>Co>Ni>Cr>Cd. Olatayo (2014) studied the physiochemical parameters of waters in Ilaje LGA of Ondo State of which Ugbo is a part. Basing his study on four stations for four months (corresponding to the peak of rainy season and onset of the dry season), he concluded that the parameters measured were within stipulated ranges for surface water.

**METHODOLOGY**

**Study area**

Nigeria has a coastline of 853 km bordering the Atlantic Ocean in the Gulf of Guinea. It is bordered to the North by the Republics of Niger and Chad, Republic of Benin at her West, to the East by the Republic of Cameroon and by the Atlantic Ocean in the South
The activity of these villages often contributes to the pollution being investigated in the Ugbo waterway. The total brackish area is estimated to cover about 12,940 km² with the mangrove comprising 9700 km², and saline swamps of the Niger Delta occupying 750,000 hectares (Figure 1a).

About 20% of Nigeria's population inhabits coastal cities, towns, and villages. The activity of these villages often contributes effluents to the waters that border their towns as in the case of Mahin/Ilaje coastal area - of which the study area forms a part (Figure 1a). Aquatic ecosystems are generally vulnerable to pollution as they receive the waste materials and sewage/effluents from the nearby sources - from rivers and from the sea. Estuaries, the transitional zone between sea and rivers are no exception (Keser et al., 2005; Kessarkar et al., 2009; Lipp et al., 2001; McCain et al., 1988).

**Sample collection**

Sampling was conducted following a predefined profile and sampling stations were selected based on proximity to the source of the pollution being investigated (Figure 1b). The sampling was done on a small hydrographic boat 23-seater capacity; 200 HP outboard engine with hydraulic steering system mounted with a Single beam SDE-28 Echo sounder (Furuno 6" Model LS-6100) for determination of sampling depth. Sampling was conducted on the 31st of March 2017 at mid-day when traffic on the waterway is slowed down. Sampling stations were established at about 200 m interval along the Ugbo waterway. In-situ physicochemical assessment of the waterway was also carried out simultaneously using a multi parameter water analyser (HANNA HI-9828 Multiparameter Water Analyser with GPS and 20 m probe). This equipment measures physicochemical parameters of water (dissolved oxygen, total dissolved solid, salinity, temperature and conductivity) on the surface and at depth up to 20 m; it also measures coordinates of sampling positions when logged. A locally fabricated sediment grab was used to collect surface sediment samples into labelled sample bags (two per station) lined with aluminium foil. The samples were then placed in ice coolers and transferred into a refrigerator at the base station prior to analysis.

**Sample analysis**

Sediment samples for each station were collected separately for TPH and trace metal analysis. Some quantity of sodium sulphate was mixed with 5 g each of the sediment samples collected for TPH analysis in a mortar with pestle, to remove moisture. The extraction of the homogenised mixtures was carried out in a separatory funnel using n-hexane and the extracts were concentrated to about 1 ml by evaporation and ready for clean-up. The clean-up and separation of the extracts was done in a glass column packed with glass-wool and silica gel slurry (dichloromethane + silica gel) with anhydrous sodium sulphate on top. The column was activated with 20 ml of n-hexane. The concentrated samples were each mixed with 2 ml of cyclohexane and introduced into the column. The samples were eluted with 20 ml of n-hexane. The eluted samples were concentrated by evaporation to 1 ml (Jiandi et al., 2015; Adeniji et al., 2017). The concentrates were analysed using GC-FID (LAWI, 2011; Cortes et al., 2012), at the Nigerian Institute of Oceanography and Marine Research, Nigeria. The concentrates were determined by the gas chromatography (AGILENT 7890A GC-FID) coupled with flame ionization detection, using a HP-5 fused silica capillary column (30 m x 320 um x 0.25 um), injecting 1 µL
sample in split less mode at 250°C. The carrier gas was helium at flow rate of 1 ml/min, average velocity of 29.47 cm/s and the detector temperature was 325°C. The column temperature was set at 60°C hold for 4 min and then increased to 320°C at 5°C/min. The concentration of TPH in the sediment samples was calculated from the chromatogram in mg/kg (Alinnor et al., 2014).

For the trace metal analysis, sediments were air dried for two days in the laboratory and later oven dried at 105°C until there was no further change in weight. Each dried sample was crushed with a pestle and mortar to homogenize. 1 g each of the homogenized samples were wet digested using 15 ml 2:1 HCl: HNO₃ of aqua regia on gentle heat on a hot mantle until the dense brown fumes began to appear. 20 ml of concentrated HNO₃ was then added. Hydrogen peroxide was also added drop wise to clear the brown fumes and improve the dissolving power of nitric acid. Digested sediments solution was evaporated to about 5 ml, cooled and filtered (using Whatman No 42 filter paper) into 100 ml different clean and dry volumetric flask and then diluted to the mark with distilled water. The digested samples were each analyzed for Pb, Ni, Mn, Zn, Cd, Fe, and Cu, using atomic absorption spectrophotometer (Model AA320N).

Stock solutions of 1000 ppm for each metal were prepared from analar grade of the granulated metal salts of high purity (99.9%). Each of the metal salt was first dried at 105°C, cooled in desiccators prior to weighing and transferred into 1 litre volumetric flasks. Equivalent gram of each metal salt for preparation of 1000 ppm of Pb, Ni, Mn, Zn, Cd, Fe and Cu solutions were dissolved in 2% (v/v) HNO₃ and diluted to volume in a 1-L flask to make a standard solution. Calibration curves were obtained with optimized instrument conditions (Turkmen and Ciminli, 2011).

RESULTS

Insitu- physicochemical parameters showed average values of 29.77°C for temperature, 108.29 ppm for Total dissolved solids (TDS), 0.10 PSU for salinity, 2.64 mg/L for dissolved oxygen (DO), 6.04 for pH and 222.8 Ωm for conductivity (COND). Table 1 presents the physicochemical parameters at each sample station K1-K7. Study area is weakly acidic with pH values between 5 and 6.7. Figure 2 and Table 2 shows the concentration of TPH in the sediments across the sample stations with an average value of 0.131 mg/Kg.

Trace metal concentrations in the sediment samples are presented in Figure 3 and Table 3 for each sample station K1-K7. Cu shows an average value of 0.093, Fe 0.845, Ni 0.067, Cd 0.032, Mn 0.064, Zn 0.137 and Pb 0.245 mg/kg. The trace metal concentration is in the decreasing order of magnitude of the different metals Fe>Pb>Zn>Cu>Ni>Mn>Cd.

DISCUSSION

The TPH values for the sediment samples in the study area are well below the maximum permissible limit of petroleum hydrocarbons in sediment (30 mg/kg) as given by Federal Ministry of Environment (FMEnv), 1991 and Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), 2002. However, the concern is for benthic organisms that may be present in the study area which can accumulate hydrocarbons adsorbed in sediments (Benson et al., 2008; Meador et al., 1995). In the works of Macaulay (Macaulay and Rees, 2014), it is understood that the
Table 1. Physicochemical parameters per location.

<table>
<thead>
<tr>
<th>Location</th>
<th>Long °N</th>
<th>Lat °E</th>
<th>Temp (°C)</th>
<th>TDS ppm</th>
<th>Salinity (psu)</th>
<th>DO (mg/L)</th>
<th>pH</th>
<th>COND Ωm</th>
<th>DEPTH m</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>6.14187</td>
<td>4.79368</td>
<td>29.28</td>
<td>191</td>
<td>0.18</td>
<td>2.17</td>
<td>6.17</td>
<td>383</td>
<td>2.4</td>
</tr>
<tr>
<td>K2</td>
<td>6.1445</td>
<td>4.79471</td>
<td>29.7</td>
<td>133</td>
<td>0.13</td>
<td>2.62</td>
<td>6.16</td>
<td>296</td>
<td>6.4</td>
</tr>
<tr>
<td>K3</td>
<td>6.14748</td>
<td>4.79529</td>
<td>29.91</td>
<td>95</td>
<td>0.09</td>
<td>2.91</td>
<td>6.02</td>
<td>192</td>
<td>5.4</td>
</tr>
<tr>
<td>K4</td>
<td>6.1495</td>
<td>4.79526</td>
<td>30.21</td>
<td>90</td>
<td>0.09</td>
<td>3.34</td>
<td>6.12</td>
<td>187</td>
<td>6.9</td>
</tr>
<tr>
<td>K5</td>
<td>6.15158</td>
<td>4.79496</td>
<td>30.01</td>
<td>92</td>
<td>0.09</td>
<td>2.92</td>
<td>6.02</td>
<td>183</td>
<td>2.9</td>
</tr>
<tr>
<td>K6</td>
<td>6.15285</td>
<td>4.79488</td>
<td>29.59</td>
<td>97</td>
<td>0.09</td>
<td>2.29</td>
<td>5.96</td>
<td>192</td>
<td>2.5</td>
</tr>
<tr>
<td>K7</td>
<td>6.15457</td>
<td>4.79448</td>
<td>29.68</td>
<td>60</td>
<td>0.06</td>
<td>2.22</td>
<td>5.81</td>
<td>120</td>
<td>2.3</td>
</tr>
<tr>
<td>K8</td>
<td>6.17831</td>
<td>4.80859</td>
<td>29.72</td>
<td>247.5</td>
<td>0.24</td>
<td>5.87</td>
<td>7.30</td>
<td>494.83</td>
<td>1.90</td>
</tr>
</tbody>
</table>

*** Reference study area used for comparison. From 0-2 cm depth (Olatunji and Ajayi, 2016). Values are given in ranges.
--- Data unavailable. K8 is the control station.

Figure 2. TPH concentration per location. K5 is the Ugbo jetty.

effect of an oil spill may be direct- affecting the organism in its immediate habitat or indirect- bioaccumulation, migration, loss of prey or predator etc.

The spatial distribution of TPH is not uniform; it varies radially outward from the point source. This could be due to the flow of current and prevailing wind direction. PMS contains low carbon fraction aliphatics and aromatics hydrocarbons and these low carbon fraction hydrocarbons evaporate rapidly from the surface of the sediments and the overlying water column. They therefore do not persist in the environment (Imaobong and Prince, 2016) and this may account for the low concentration of TPH in the sediments.

In order to determine the significant effect of the discharge of the PMS on the environment, the comparison of the TPH from the present study with values reported in other parts of Nigeria and some parts of Africa outside is presented in Table 4. TPH levels in the present study are much lower than the concentrations reported from other study areas adopted for comparison. The highest mean concentration of TPH (53500 mg/kg) occurs in sediment samples from the Gulf of Mexico where the studies was carried out during/after the BP/Deepwater Horizon oil spill (April, 20 to July, 15 2010) (Paul et al., 2013). Relatively high mean value (41900 mg/kg) occurs in sediment samples from Benin River which is adjacent to a lubricating oil factory (Samuel and Ayodele, 2014). Values of 1602 and 1320 mg/kg also occur in Ubeji River in Warri Nigeria, part of the oil producing area of the country (Adewuyi et al., 2011) and on Sudannese Red sea coast (Portsudan harbour and Bashayer Marine Terminal on Sudannese Red Sea coast).
Table 2. TPH concentrations in sediment.

<table>
<thead>
<tr>
<th>Sample Stations</th>
<th>Total Petroleum Hydrocarbon (TPH) in sediments mg/ Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>0.1398</td>
</tr>
<tr>
<td>K2</td>
<td>0.1373</td>
</tr>
<tr>
<td>K3</td>
<td>0.1368</td>
</tr>
<tr>
<td>K4</td>
<td>0.1167</td>
</tr>
<tr>
<td>K5</td>
<td>0.1466</td>
</tr>
<tr>
<td>K6</td>
<td>0.1208</td>
</tr>
<tr>
<td>K7</td>
<td>0.1203</td>
</tr>
</tbody>
</table>

Table 3. Trace metal concentrations per location in mg/kg.

<table>
<thead>
<tr>
<th>Sample station</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Cd</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>K1</td>
<td>0.380</td>
<td>0.082</td>
<td>0.043</td>
<td>1.623</td>
<td>0.046</td>
<td>0.019</td>
<td>0.095</td>
</tr>
<tr>
<td>K2</td>
<td>0.403</td>
<td>0.178</td>
<td>0.095</td>
<td>0.754</td>
<td>0.090</td>
<td>0.017</td>
<td>0.065</td>
</tr>
<tr>
<td>K3</td>
<td>0.242</td>
<td>0.107</td>
<td>0.135</td>
<td>0.570</td>
<td>0.182</td>
<td>0.120</td>
<td>0.002</td>
</tr>
<tr>
<td>K4</td>
<td>0.230</td>
<td>0.132</td>
<td>0.084</td>
<td>0.782</td>
<td>0.040</td>
<td>0.016</td>
<td>0.077</td>
</tr>
<tr>
<td>K5</td>
<td>0.210</td>
<td>0.163</td>
<td>0.157</td>
<td>0.793</td>
<td>0.034</td>
<td>0.013</td>
<td>0.092</td>
</tr>
<tr>
<td>K6</td>
<td>0.140</td>
<td>0.128</td>
<td>0.094</td>
<td>0.651</td>
<td>0.041</td>
<td>0.025</td>
<td>0.063</td>
</tr>
<tr>
<td>K7</td>
<td>0.110</td>
<td>0.172</td>
<td>0.043</td>
<td>0.741</td>
<td>0.033</td>
<td>0.015</td>
<td>0.052</td>
</tr>
<tr>
<td>K8</td>
<td>0.036</td>
<td>0.072</td>
<td>0.021</td>
<td>0.339</td>
<td>0.024</td>
<td>0.000</td>
<td>0.022</td>
</tr>
<tr>
<td>***</td>
<td>29.0 - 1646.0</td>
<td>112.0 - 10001</td>
<td>13.0 - 861.0</td>
<td>3.0 - 219.0</td>
<td>3.0 - 219.0</td>
<td>3.0 - 219.0</td>
<td>3.0 - 219.0</td>
</tr>
</tbody>
</table>

**Reference study area used for comparison. From 0-2cm depth (Olatunji and Ajayi, 2016). Values are given in ranges. Data unavailable. K8 is the control station.**

Figure 3. Trace metal concentration per location. K5 is the Ugbo jetty.

(Aishah et al., 2013) respectively. But low range of concentration occurs in sediment samples from Algoa Bay, Eastern cape South Africa (0.72 to 27.03 mg/kg) (Abiodun et al., 2017) and coastal area of Papar and Putatan, Sabah Malaysia (0.52 to 4.59 mg/kg for Papar and 0.26 to 1.64 mg/kg for Putatan). High level of
The need therefore for biota; this is particularly true for the benthic animals, bioaccumulation through the food chain consumption or intake of trace metal by plant roots and the oil producing and maritime activities. Transportation activities, discharge of sewage and other industrial effluents into the coastal water bodies such as occurs in the case for Algoa Bay, coastal area of Papar and Putatan, Sabah Malaysia and the present study area does not result in high hydrocarbon contamination. Physicochemical data obtained in the study area show high dissolved oxygen (DO) values at K8 (the control station) which more than doubles the values obtained across the stations K1 to K7. This result is indicative of the effect TPH presence has on the study area. In addition, total dissolved solids (TDS) values are also highest at K8 and decrease as we move downstream, only to increase away from K5 suggesting a radial distribution.

The highest concentration of the trace metals occurs for Fe followed by Pb across sampling stations. The spatial distribution of the trace elements in the sediment samples varies with the different sampling stations. The general trend for trace metal distribution increases downstream. Highest values are collected at K1. However, this increase is also observed at k6 and K7 indicating a radial increase. The prolonged presence of heavy metals in the sediment samples from Ugbo-Ilaje area, might affect aquatic life in three ways, direct consumption or intake of trace metal by plat roots and benthic animals, bioaccumulation through the food chain and release of the accumulated trace metals into solution as the overlying water becomes anoxic (Olatunji and Ajayi, 2016). The weakly acidic nature of the overlying water will imply that these metals could be easily taken into solution and absorbed by aquatic organisms.

Trace metal concentrations in sediment from the study area were compared with results published by Olatunji and Ajayi (2016) from 4 wetland areas in Lagos. The comparison was limited to the first 0 – 2 cm depth in the Lagos area. Far higher trace metal concentrations were reported for the Lagos location than those of the present study. However, several factors could have contributed to the measurements observed at the Lagos location.

## Conclusion

This study has shown that concentration of TPH in the sediment samples from the Ugbo water is very low. Although this may result to say that the activity of offloading PMS into barges at the Jetty have very little impact on the environment in terms of TPH contamination, the concern is for benthic organisms that may be present in the study area which can accumulate hydrocarbons adsorbed in sediments; the need therefore for biota monitoring in the environment. Furthermore, the TPH films on the water surface often prevent dissolution of oxygen at the water surface leading to anoxia.

From the study area, we can conclude that the study area is polluted and currently the degree of pollution is not alarming. We arrive at this conclusion based on the presence of TPH concentrations in the sediments albeit, in minute amounts. However, a regular monitoring of water, sediment and tissue of aquatic organisms in the area should be done for TPH and trace metal concentrations. In addition, there is a need to raise awareness on the dangers of consuming the water or the risk to aquatic life should the usual practice continue even as the pollution rate is not alarming. The people in the community should be discouraged to dispose of their waste in the water body; alternate waste disposal methods should be introduced and monitored. Further research works should be carried out to study the effects of trace metals on the people of Ilaje region, especially on the people of Ugbo, Ugbonla, and Ode-Ugbo whose agricultural lands are irrigated by the water. Agricultural waste should not be directly disposed into the water body and for this purpose. Also, the government should pay attention to improve the water quality of Ilaje coastal communities, which should also consider trace metals.

A clean-up plan should be mapped out for cleaning up the area before the concentrations increase to an
alarming degree. Health practitioners in the area should be trained in rapid response techniques and early detection methods. Also, medical supplies to tackle illnesses resulting from this pollution should be made available since these symptoms might be alien to the area prior to this.

CONFLICT OF INTERESTS
The authors have not declared any conflict of interests.

ACKNOWLEDGMENT
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REFERENCES

Full Length Research Paper

Sustainability of Chiredzi town water supply and wastewater management in Zimbabwe

F. Homerai¹, A. W. Mayo¹* and Z. Hoko²

¹University of Dar es Salaam, Water Resources Engineering Department, P. O. Box 35131, Dar es Salaam, Tanzania.
²University of Zimbabwe, Civil Engineering Department, P. O. Box MP167, Mount Pleasant, Harare, Zimbabwe.

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Urban water supply and sewage coverage in Zimbabwe is currently estimated at 78 and 73%, respectively with unserved population relying on boreholes and pit latrines. However, no study has been conducted to assess how small towns, such as Chiredzi, are sustaining their systems despite limited funding from the Government. A study was carried out to assess the sustainability of Chiredzi town water supply and wastewater management systems in Masvingo, Zimbabwe. The study assessed the level of service provision, level of users’ participation and sustainability of water supply and wastewater systems. Data was collected through household questionnaires, key informant interviews, focus group discussions, desk study, water and wastewater analysis results, and field observations. A total of 150 households were interviewed and Statistical Package for Social Science, Microsoft Excel Spreadsheet, and De Carvalho Sustainability index were used as tools to analyse data. The service coverage was below the target of 100 and 80% for water supply and sewage coverage, respectively. The study revealed that 55.3% of the respondents were not satisfied with the level of services provided. Stakeholder participation was found to be done through contribution of ideas and reporting pipe burst with very few contributing money. The overall sustainability was found to be 6.5, a category of satisfactory progress towards sustainability. Finally, the findings showed that there is great need to improve on technical, social and financial aspect.

Key words: Level of service provision, stakeholders participation, sustainability index, water supply, wastewater management.

INTRODUCTION

Water supply and sanitation sectors are among the key aspects of human health and development of a country (Eid, 2015). In 2015, 193 member states of the United Nations adopted the 2030 Agenda for Sustainable Development, which comprises 17 Sustainable Development Goals (SDG) and 169 targets that seeks to end poverty, ensure prosperity for all people and protect the planet (United Nations, 2015). SDG target 6.1 seeks to achieve universal and equitable access to safe and affordable drinking water for all by year 2030 and SDG target 6.2 intends to achieve access to adequate and equitable sanitation and hygiene for all and by the end of
the same year. In accordance with WHO and UNICEF (2017), Sub-Saharan Africa, Zimbabwe inclusive, is lagging behind in as far as progress towards the achievement of SDG targets 6.1 and 6.2 are concerned. It is estimated that only 58% of population in Sub-Saharan Africa used at least a basic drinking water service in 2015, although the global average was 89% (WHO and UNICEF, 2017). In the same report, it was estimated that 28% of Sub-Saharan Africa population used at least basic sanitation services in 2015, which was much lower than the global average of 68%.

Zimbabwe had highest coverage of 97% levels in Africa, for both urban water supply and sewerage networks after independence (1980) up to 2000 (World Bank, 2009). WHO and UNICEF (2017) estimated that in 2015, 77% of Zimbabweans had improved water supply, but only 37% had improved sanitation facilities. An "improved" drinking-water source is the one that is constructed in a manner that adequately protects the source from any external contamination, particularly faeces. On the other hand, an "improved" sanitation facility is one that hygienically separates human beings from coming into contact with human excreta. Facilities that lack these qualities are considered "unimproved" (WHO and UNICEF, 2012).

The provision of improved water supply and sanitation facilities in urban areas have gradually deteriorated from 100% in 1990 to 97% in 2015 and 52% in 1990 to 49% in 2015, respectively (WHO and UNICEF, 2017). As a result, Zimbabwe recently suffered one of the worst cholera outbreaks recorded in sub-Saharan Africa (WHO and UNICEF, 2010). In accordance with Manzungu (2012), Zimbabwe cannot achieve targets for improved water supply and sanitation of reducing the number of people without access to water and sanitation by 50%. This is because of a number of factors including the growing demand from its growing population (Watson, 2009), melt-down of Zimbabwe’s economy (Homerai, 2015), the willingness of foreign aid organization to avail funds to build and finance infrastructure projects (World Bank, 2009). Other challenges include implementation of low cost sewage treatment that at the same time permit selective reuse of treated effluents for agricultural and industrial use (Arth, 2012). Zimbabwe population has nearly doubled from 7.2 million people in 1980 to about 13 million in 2012 (Zimstat, 2012).

In accordance with UNICEF and USAID (2009), public works systems in the developing countries have long been recognized as complicated and disorganized. In Zimbabwe, most investments towards rehabilitation of infrastructure are focusing on large cities such as Harare, Bulawayo and Mutare, but according to UNICEF (2010) populations in the country’s small towns have been growing rapidly. Consequently, this has placed a huge burden on the water supply and wastewater systems infrastructure in these small towns. Nhapi (2009) suggested that there are limited human and financial capacities in urban towns to provide efficient water services.

In Chiredzi town, about 65% of the residence have no access to safe water due to pipe bursts, failure of the water treatment plant and at times due to rationing and power cuts. As a result, frequent outbreak of cholera in Chiredzi town may be caused by the failure of the authorities to provide safe and reliable water to the public (Homerai, 2015). The government of Zimbabwe is now subsidizing water supply and sanitation services in large cities like Harare and Bulawayo, but small towns such as Chiredzi have not received similar attention. This study seeks to investigate the sustainability of water supply and wastewater management systems in Chiredzi town.

MATERIALS AND METHODS

Description of the study area

Chiredzi Town, which covers 128 km², is located in the south-east part of Zimbabwe in Masvingo Province at coordinates, 21°02'20"S and 31°40'40"E (Figure 1). In accordance with ZimStat (2012), the town’s population was 30,594 people in 2012, and is estimated to have a current population of about 34,300 people in 6866 households with a yearly growth rate of 3.9%. Chiredzi town was established in 1957 as Crown Township for the sugar and citrus estates and granted town status in 2002 with 8 wards. The annual average temperature is 22°C and is characterized by low and erratic rainfall (Unganai, 2008). The town is small and has one major industry, Delta Chibuku Breweries, a Dairy board and is surrounded by sugar cane producing estates, which include Triangle, Hippo Valley, Mkwasine and smallholder farmers, which require large volumes of water for irrigation and domestic use.

The raw water source, which is abstracted from Lake Mirkwi, was completed in 1960 and pay Zimbabwe National Water Authority (ZINWA) for the bulk supply (Homerai, 2015). The lake also supports water schemes for several farmers and large sugar cane irrigation schemes in Triangle and Hippo Valley Estates. The town’s treatment plant, which consists of coagulation, flocculation, sedimentation, filtration and chlorination, was commissioned in 1964 and its infrastructure has since deteriorated. The plant was designed to produce 10 ML/day, which has gone down to an average of 3.5 ML/day, which is only achievable when the plant is running for 24 h. Chitsangan Reservoir with a capacity of 1000 m³ was also decommissioned due to a broken drain pipe that was causing leakages. Chiredzi town uses waste stabilisation ponds for its wastewater treatment. The first set of ponds was established at Khonami, which have been decommissioned due to town expansion paving way for a new set of ponds. Since then these ponds have not being desludged resulting in overloading. United Nations Children Education Fund (UNICEF) intervened to mitigate the epidemic by drilling 15 boreholes, but only 8 boreholes are still functioning. However, the groundwater has high mineral content such that the water is hard and difficult to drink (Homerai, 2015).

Study design and data collection

Information for water supply and wastewater management systems was collected from the institutions responsible for town water supply and sanitation and the stakeholders involved. Both quantitative and qualitative data was obtained from household survey, focus group discussion, key informant interviews and physical observation. Primary data was obtained from households, Chiredzi Town Council, Hippo Valley Estates officials and Environmental Health
Technicians. Secondary data was obtained from annual reports and inventories.

Qualitative data were used to collect data based on facts from an individual point of view. Attitudes, perceptions and knowledge of stakeholders with regards to service delivery were assessed. Qualitative methods were conducted in a natural setting, without intentionally manipulating the environment. Probability and non-probability sampling techniques were employed to select study area and study sites. Purposive sampling was used to identify the areas in Chiredzi town under study. Systematic convenience sampling was used to select the households which were interviewed as suggested by Depoy and Gitlin (2005). Only households willing to participate in the research were interviewed. Purposive and systematic sampling techniques were employed to identify key informants and households to be interviewed, respectively.

Data on sustainability of water supply and wastewater management systems of Chiredzi town was obtained from desk study, personal observations, water and wastewater quality analysis, household surveys, key informant interviews and focus group discussions to collect both secondary and primary data. The information was compiled and analyzed on continuity or hours of water availability per day, population served, coverage of the utilities, water consumption and production and level of service provision.

Physical inspection was carried out on water supply and treatment plant along with wastewater stabilization ponds structures to determine the quality and physical condition of the facilities. Main aspects assessed under physical condition are the overall functionality of the water supply and treatment plant along with wastewater stabilization ponds. Other aspects such as easiness of operation, breakdown rate and the staff level of education, monitoring of water quality at different sites such as at water treatment plant, storage tanks and at the end user’s tap will be observed.

Water samples were collected at taps, and were analyzed onsite for electrical conductivity and pH. Conductivity meter model WTW Cond7110 was used to analyze electrical conductivity (EC) whilst the Ecosan pH 5/6 mv/pH meter is to be used to measure pH. Samples of domestic wastewater were collected at the effluent.

Water supply and sanitation was assessed and evaluated from the maps of water supply and sanitation networks taking into consideration leak detection and response time, shortage of water, frequency of occurrence of faults and other options for both water and sanitation provisions while undergoing repairs. Sanitation facilities were visited and assessed in terms of their capacities considering population growth and the method used.

Interviews were conducted and the respondents are informed about the current problems and policies designed to solve the problem. Wherever opinion of the water users was required, the sample sizes for questionnaires were determined using Equation 1 in accordance with Krejcie and Morgan (1970).

$$n = \frac{\chi^2 \times p \times (1-p) \times N}{e^2(N-1)+Z^2 \times p \times (1-p)}$$  \hspace{1cm} (1)

Where \(n\) is the required sample size, \(N\) is the population size, \(p\) is the population proportion, which is assumed to be 0.50 since this would provide the maximum sample size and \(\chi^2\) is the the table value of chi-square for 1 degree of freedom at the desired confidence level of 0.05. The degree of accuracy \(e\) of ±5% was used hence a confidence level of 95%. Systematic convenience sampling was used to select households which were interviewed. A total of 150 questionnaires were administered on both high and low density wards.

Structured, semi-structured, and open-ended interview guidelines were developed and used to generate relevant data from the local authority offices, humanitarian organizations and Health Office. The local authority provided information on the roles of the department, water issues, factors affecting sustainability of water supply and treatment, along with wastewater management systems. The Environmental Health Technician from the Health Office provided
information on safe disposal of wastewater and monitoring of water quality. Data on financial management, operation and maintenance, women participation, along with management of water supply and wastewater was obtained through interviews with local authority offices and water users.

Focus group discussions were held using discussion guide with women, men and water committee members comprising 12 people as recommended by Robinson (2002). The collected information included selection of water residence committees, decision-making on operation and maintenance, challenges facing the communities, women participation, availability of external support and coordination between the residents and services providers, trainings undertaken and their views on the solutions to water problems.

Data analysis

The primary data collected from household survey through structured questionnaires were first checked for accuracy and data entries were coded. Thereafter, data were entered, edited and analyzed using statistical package for social science (SPSS) version 16.0 software. Data were explored for frequency of responses, distribution trends and statistical relationships. Responses from the key informant interviews were used to validate the responses of the households. The level of services of the water and wastewater stabilization pond system were analyzed by assessing the services in terms of coverage, population served, water quality and quantity, wastewater characterization, and the capacity of utilities to serve the town. Laboratory analysis of water and wastewater was done. Water demand (present and future) for domestic, commercial, institutions, industries to be calculated and projected from 2015 to 2040 was analyzed using Excel. Water deficit was calculated from water production and demand data. SPSS was used to analyse field survey data on residence perception on service delivery.

Sustainability analysis

The use of sustainability indicators is recommended for evaluating the sustainability of water supply and wastewater management systems as it allows for a comprehensive evaluation of the environmental, economic and socio-cultural dimensions (UNEP, 2003). The indicators include physical conditions, operations and maintenance, consumer satisfaction, financial management (cost recovery) and willingness to sustain the services. Water demand and wastewater management aspect are selected based on population growth due to urbanization in developing countries, which has become a challenge to water supply and sanitation services (Watson, 2009). The sustainability index was obtained from sustainability aspect sub-indicators. For each sustainability aspect, sub-indicators were measured using series of questions assessed through semi-structured interviews, focus group discussion, measurements, observations and household surveys. Aggregated scores/100 was expressed for each sustainability indicator, which is technical, social, financial and environmental sorted fewer than four key factors of sustainability.

Core-indicator = Σ(sub-indicator *Weight)  

(2)

Technical aspect scoring was based on a series of questions from 10 technical evaluation questions and also from information from the town council record books. The scores measure the level of service offered by service provider. A perfect technical score indicates that the water supply and wastewater systems are providing adequate services to the users and the systems are working perfectly, which means there is high service coverage, water production matches water consumption and water losses are minimum. The financial management scoring was based on 19 questions from key informant with the Financial Department of Chiredzi Town Council. The perfect score would indicate that the town council is able to cover costs incurred during operation as well as maintenance and services provision. It indicates also that there is savings for future repairs and system upgrading. It also reflects on high cost recovery and capacity of the users to pay for the services.

Environmental management scoring was based on 5 evaluation questions from the Department of Environmental Protection of Chiredzi Town Council. This measures the treatment efficiency of both water and wastewater and how the quality is monitored. It also measures the safe disposal of wastewater in natural waters, that is, the extent of pollution and also the extent of reuse. A perfect score would reflect high treatment efficiency of the systems, plus safe disposal of wastewater and desludged faecal matter into the environment.

Social aspect scoring was based on a series of 7 questions from the household questionnaires. The indicators measure the people’s perception on level of services by the service provider, whether they are satisfied or not. A perfect score would reflect that the systems can provide adequate services to the users. This also reflects that there is high level of services, consumer satisfaction along with awareness and education.

The sustainability index for a particular city (Si) is the sum of all the weighted components (Equation 3). Indicators and sub-indicators are aggregated in the same manner as components. The standardized value of the respective component \( X_i \) is multiplied by the attributed weight, \( w_{ij} \), to give a value on a scale of 0 - 10. De Carvalho (2007) equation was used to calculate sustainability index for Chiredzi Town.

\[
SI_i = \frac{\sum_{i=1}^{N} w_{x,i} x_i}{\sum_{i=1}^{N} w_{x,i}} = w_s S + w_F F + w_T T
\]

(3)

Where \( W_s \) is the weight for social (S) aspect, \( W_F \) is the weight for environmental (E) aspect, \( W_T \) is the weight for financial (F) aspect and \( W_T \) is the weight for technical (T) aspect. The overall sustainability index of Chiredzi town is an average of the 4 indicators which was adjusted to a 10-score scale each with equal weight of 25%. The project is considered sustainable if the sustainability index is above 6.67, potentially sustainable if index is between 5 and 6.67 and unsustainable if index is below 5.

RESULTS AND DISCUSSION

Demographic characteristics of respondents

The interview involved 77 men (51.3%) and 73 women (48.7%). In terms of level of education, the survey showed that 98% of the respondents completed primary education with at least 12.7, 26.7 and 58.7% found to have attained primary, secondary and college education, respectively. Only 3 out of 150 respondents did not attain formal education. This made the household survey credible because most of the respondents were able to read the questions and give accurate information. With regards to age structure, 88.7% of the respondents were
in economically active age group of 20-50 years. The major sources of income of the respondents was employment by either government or private sector (54.7%), informal business, which includes selling food and vending (31.3%), formal businesses (8%) and the least was small scale farming (6%). When respondents were asked about the monthly household income, most of them did not give exact answer due to lack of records and others were reluctant to expose their real income. Those who are into informal business gave estimations of what they sell to raise money for their household needs. Crops like maize and beans, and plantations were cited as their main sources of income to the farmers. From those who were able to state their incomes, the monthly income of the household ranged from USD100 to USD700. About 50.7% of the respondents have income below poverty datum line of USD 400 for a family of 6 and only 20% of the families have income exceeding USD 600.

Water supply services

About 5120 out of 6576 properties (77.9%) are connected to water supply network of Chiredzi town. This water supply services coverage is lower than the target coverage of 90% (Water Operators Partnership, 2009). The residents who are not connected to water supply system are depending on shallow wells for their water needs. However, it was noted that Chiredzi town is better than other urban areas in the region, such as Beira of Mozambique which has coverage of as low as 12%. However, other cities such as Walvis Bay of Namibia and South African urban areas have coverage of as high as between 90 to 100% (Water Operators Partnership, 2009). With the population growth rate of 3.9%, Chiredzi town is expected to have a population of 50,000 people in 2025. In accordance with Chiredzi Council Report (2014) per capita water demand is estimated to be 200 L/day, which can be met with installed plant capacity of 10,000 m³/day. The water demand projection shows that up to year 2025 there will be enough water supply, but thereafter the system would need upgrading to meet the demand. The growth for both commerce and institution was assumed to be 1% because of Zimbabwe’s economic crisis. At the moment, the plant can produce 7,853 m³/day against the estimated consumption of 6,863 m³/day. A person in African cities requires 20-50 L of water to ensure basic needs of drinking, cooking and washing (Minghong and Pelin, 2012). Taking this into consideration, the utility is providing enough water to the users.

Response from residents and field observation shows that water is supplied by pumping directly to the consumers for 8 h/day because Chitsanga Reservoir was decommissioned. Water is also pumped to Chigarapasi Reservoirs for 6 h daily. Most South African and Walvis Bay of Namibia utilities provide water for 24 h daily. Availability of water, according to Nair (2010) is very essential in the provision of water for each person and must be sufficient and continuous for domestic and personal uses. Therefore, Chiredzi town water users are deprived of this human right by supplying water intermittently, which causes supply pressure losses, sewer system blockages and inequities in the distribution of water (WUP, 2001).

Among many factors that affect the quality of service delivery, is the reliability of the systems. About 98% of water consumers store water because water supply is intermittent. The users were also complaining of lack of information prior to interruption of the service. Data collected from the field over a period of two months indicates that the average period between the stopping of pumping and the resumption of pumping after breakdown, servicing the plant or back flushing, varies from 0.5 to 3.5 h with an average of 2 h daily. According to Hoko and Hertel (2006), the downtime for water utility should not be longer than 2 days.

Water management

Out of 6576 properties in Chiredzi town, about 6524 are metered, which is equivalent to 99% of meter coverage. However, field observations and key informant interviews have shown that only 25% of the meters are functioning at the time of the study. Therefore, about 75% of the customers are billed monthly based on estimation, which is potentially inaccurate. The information obtained from town council records and key informant interviews from technical department, shows that Chiredzi town water supply has non-revenue water losses of about 65%, which include 20% real losses through leakages during transmission and distribution. The apparent losses such as illegal connections, water theft and inaccuracies in meter reading are estimated to be 45%. Inaccuracy of meter reading was also evident as with the use of return valves at the plant, wrong figures were recorded at times due to reverse movement of water when the valve is faulty and the plant is not pumping. This information matched that of key informant interviews where it was highlighted that burst pipes take two days or more to repair. Mal-functioning meters also contributed to high percentage of non-revenue water.

Metering of users is considered to be good practice as it allows them to have confidence in the service provider and provides water utility tools and information for better management of the systems (Homerai, 2015). Metering helps in water conservation, leaks detection, and problem in the distribution process when conducting a system audit (AWWA, 2006; Hogas et al., 2016). In developing countries, non-revenue water should be kept below 23% according to Tyman and Kingdom (2002). This showed
that the council is billing less water than is produced, which suggests that the Council must fix mal-functioning meters and attend to the leakages and theft in time to reduce non-revenue water losses.

Water quality monitoring

The results of water analysis of the measured parameters are within Association of Zimbabwe Standards SAZS 560-1997 limits and WHO guidelines because water was free from disease causing micro-organisms and chemicals substances that are a threat to human health (Table 1). According to David (2005), water quality and quantity are considered important factors in rating the performance of a water supply system. Records from the water treatment plant indicates that a thorough monitoring system of the water quality is practiced once a month from domestic points and after every 2 h for pH, temperature and residual chlorine in the treatment plant. Residential taps are randomly selected for water quality analysis. About 80% of the respondents were satisfied with the quality of water.

Wastewater management

It was observed that 4779 out of 6579 properties (72.6%) were connected to sewage network. Other common sanitary facilities include VIPs and pit latrines (21.4%) as well as septic tanks and soakage pits (6.0%). From the survey, 27.4% households use on-site sanitary facilities and this constitutes the low density suburbs and illegal settlement properties. This reflects that the town is lagging behind in terms of sewage services coverage which was targeted to reach 82% by year 2015 (Water Operators Partnership, 2009). It was noted that Southern region have the highest coverage for sewerage, with Walvis Bay of Namibia having 100% coverage. In the Eastern region it was found that Moshi of Tanzania has coverage of 44%. This reflects that even Chiredzi town is lagging behind its set target to achieve 100% sewerage coverage as compared to Lusaka (Zambia) with 11% coverage. With the assumed population growth rate of 3.9%, the current population would be 34,315; implying that daily waste generated is 2,607 m$^3$/day, which suggests that the design can sustain influent loading over the next 25 years.

Wastewater analysis results show that the measured parameters are within Environmental Management (Effluent and Solid waste Disposal) Regulation, 2007 limits (Table 2). Arth (2012) emphasized the need for effluent quality to be of World Health Organization Standards to prevent environmental pollution and spread of diseases. Reports from the authorities show that examination of domestic wastewater is done for all parameters on monthly basis (Figure 2).

Customer care and consumer perceptions on service delivery

Respondents submit their complaints to water utility management. Others make use of resident association,
Table 2. Effluent wastewater quality analyses.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Effluent</th>
<th>Zimbabwe Standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>7.45</td>
<td>6.9</td>
</tr>
<tr>
<td>Electrical conductivity</td>
<td>µS/cm</td>
<td>618</td>
<td>&lt;2000</td>
</tr>
<tr>
<td>Sodium</td>
<td>mg/l Na⁺</td>
<td>27.78</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Potassium</td>
<td>mg/l K⁺</td>
<td>13.78</td>
<td>&lt;500</td>
</tr>
<tr>
<td>Iron</td>
<td>mg/l Fe²⁺</td>
<td>0.48</td>
<td>&lt;8</td>
</tr>
<tr>
<td>Manganese</td>
<td>mg/l Mn²⁺</td>
<td>&lt;0.01</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/l Zn²⁺</td>
<td>&lt;0.01</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Biological oxygen demand</td>
<td>mg/l</td>
<td>15</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>% saturation</td>
<td>50</td>
<td>&gt;75</td>
</tr>
<tr>
<td>Total Hardness</td>
<td>mg/l CaCO₃</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Total Suspended Solids</td>
<td>mg/l TSS</td>
<td>100</td>
<td>&lt;50</td>
</tr>
<tr>
<td>Total Dissolved Solids</td>
<td>mg/l</td>
<td>171</td>
<td>&lt;1500</td>
</tr>
<tr>
<td>Sulphate</td>
<td>mg/l SO₄²⁻</td>
<td>117</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>mg/l PO₄³⁻</td>
<td>1</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Chlorine</td>
<td>mg/l Cl</td>
<td>31</td>
<td>&lt;250</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>mg/l N</td>
<td>8.6</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Faecal coliforms</td>
<td>Number/100 ml</td>
<td>800</td>
<td>&lt;1000</td>
</tr>
</tbody>
</table>

United Chiredzi Residents and Rate Payers Association (UCHIRRA), which has committee members in each of the 9 Wards of the town. It was noted that the UCHIRRA committee members meet councilors every month to report on the service delivery issues to councilors of respective wards. In accordance with the Department of Customer Care Services, 75% of customer complaints are attended within 24 h for both water supply and wastewater systems. However, feedback from 80% of the consumers indicates that it took more than two days to attend to the complaints. The consumers were also not satisfied with reliability of water supply because of the intermittent flow. As a result, 55.3% of the respondents reported that they were not satisfied with the performance of water utility. Notification of service interruptions is of paramount importance as a customer care factor, which affects users' perception on service delivery of utilities. It was observed that only 2.7% of the respondents from the sampled households received notification prior to service interruption. It was also noted that 77.3% of the respondents mentioned that when paying bills the service personnel are helpful and friendly. However, the respondents prefer to pay their water bills through bank instead of travelling to water utility offices, which saves
Roles and responsibilities of UCHIRRA

The main responsibilities of UCHIRRA are to monitor the quality of service delivery especially on water availability, the performance of sewerage system, calling for meeting of water users when need arises, and meeting with councilors to discuss issues of service delivery. They also educate and create awareness to water users on the importance of timely payment of bills. These duties are vital to the water supply and wastewater management systems since they promote sustainable use of resources and efficient operations of the systems in as far as service delivery is concerned. According to the chairperson, the meetings were meant to assist the councilors and management of council by giving a feedback on service delivery with respect to each ward, concerning mobilizing users to pay for the bills, protection of the piping system for both water supply and sewer system to minimize bursts. It was noted that user association committees, comprising 9 members of whom 4 were women and 5 men were established in every ward. However, while the gender aspect was taken into consideration, the position of chairpersons in all 9 wards was held by men, whilst women are secretaries. Similar observations were made in Tanzania where Mayo and Nkiwane (2013) reported that 78% of leadership positions were occupied by men.

Participatory approaches are recommended when implementing water project activities because they are instrumental for sustainability of water supply projects (Dube, 2012; Kamruzzaman et al., 2013; Kwangware et al., 2014). In Chiredzi town it was observed that users participate by contributing ideas (55.3%) and cash (16.7%), but 28.0% did not participate in any way. The results matched those of Mayo and Nkiwane (2013) who found out that reporting of leakages to management help minimize water losses and improves sustainability of the water utility. According to some of the respondents, timely payment of their bills was considered a great contribution to the sustainable management of the utilities. The need to have continuous supply of water and avoiding disease outbreaks such as cholera by the households was the driving force for users to participate in the services provision, which benefits the users socially and health wise.

Focus group discussions and household questionnaire were used to assess the involvement of women in water supply and sanitation management systems. From the sampled households, 75% of the respondents agreed that women are involved although they are marginalized, particularly in leadership positions such as councilors, chairpersons and treasuries. In as far as National Gender Policies are concerned Zimbabwe is ranked 107 on related global related development index (WEDC, 2007).

This reflects the low status given to gender with respect to access, control and ownership of economic resources and decision-making positions. Therefore, there is need to address the imbalance between men and women. The Zimbabwe gender policy gives comprehensive strategies for water supply, but not for sanitation. However, water and sanitation issues are combined and guided by water and sanitation policies, but sanitation is given less attention.

Stakeholder participation in project activities is considered as very important because it builds a sense of ownership and commitment among the local people (IRC, 2003). About 54% of the respondents have participated in association meeting and about 61.3% of the respondents have contributed to the provision of services through reporting pipe bursts and sewer blockages. From the demographic information, it was found that the general meeting, which involves all members is held once annually whereas water users’ committee members hold meetings once every month. The meetings were meant to discuss the quality of service delivery in each ward and propose solutions to the identified problems. From focus group discussions it was found that water users committee meet once every month with councilors to fill in the score cards on service delivery.

Tariff setting, revenue collection and willingness to pay

From the sampled households, only 18% of the consumers were aware and involved in tariff setting, the majority of whom was council employees. This is because water tariffs are set by the government although procedural consultations were made through stakeholder meetings as confirmed by 56% of the respondents. However, it was noted that 67% of the respondents were satisfied with the set tariffs. In principle, setting of tariffs should involve participatory approach whereby stakeholders, particularly consumers are actively involved in order to positively influence willingness to pay and revenue collection (Stenekes, 2006; Murinda, 2010). Chiredzi town water utility utilizes volumetric tariff system and charges 0.30, 0.35 and 1.00 USD/m³ for domestic, institutional and commercial customers, respectively. Unfortunately, only about 25% of the meters are functioning, which means bills are largely estimated. While water tariffs for water services are depending on the location and production costs (Kaercher et al., 2004), there was no evidence that the gazetted tariff for Chiredzi town considered actual cost of development and maintaining the utility. In African small towns, government determines the charges regardless of consideration of actual cost of supplying water.

It was further observed that only about 65% of users pay their water bills, which are required to be paid within 60 days, but are rarely disconnected for failure to pay for...
the services. It is known that the town council uses fines and disconnection from service as methods to enforce payments. From this study, 93.3% of the respondents were willing to pay for the services, but 35% of the consumers had not paid their bills because of various reasons including affordability of the services, poor service provision and complaints on estimated bills in the absence of metered bills. The reconnection fines of USD 15 and USD 30 for residential and commercial, respectively are charged by the council. However, due to corrupt staff responsible for disconnection, users continue to use the service after bribing them. It was also noted that urban services are used for political gains, where the government can intervene and allow defaulters to use water services.

Chiredzi Council is operating under the Urban Council’s Act and complimenting it with the ZINWA Water Act of 1998. Urban Councils Act Chapter 29:15 governs the management of urban areas in Zimbabwe. It was noted that Part XIII: 83 of Urban Councils Act apply to water supply services with the exclusion of sanitation. It specifies the responsibilities of the council concerning the provision and maintenance of water supply within and outside council areas. The Acts’ weakness is that it does not give enough guidance for management of urban water supply services. Issues of tariff settings, punishment of defaulters and who should regulate water management in the urban areas are not addressed in the Act. Also worth noting is that Zimbabwe has no policy on urban water and wastewater services. In Southern African countries, only South Africa and Zambia have Urban Water and Sanitation Acts, which are specific to water supply and sanitation in urban areas (Murinda, 2010). The Acts clearly elaborates on the institutional arrangements, which exist in the urban areas and their roles in the management of water supply, wastewater and solid waste services.

Generally, the service level of Chiredzi town is poor because of the failure of council to rehabilitate, expand and upgrade the old and worn out infrastructure. Thus the town is lagging behind in terms of service coverage, with 77.9 and 72% for water and sewerage systems, respectively. Willingness to pay is affected by many factors especially the level of service delivery, which can increase or decrease willingness to pay for the improved services. The reliability of the service is of importance to users as this also determines the level of willingness to pay by the users. These results supported those of Bhandari and Grant (2007) who mentioned that reliability of water supply systems is among the factors which influence the willingness of users to pay for the services. In another study in Kenya, Spaling et al. (2014) reported that water supply, regulatory policy and local management are among the factors affecting the sustainability of a community water supply project. Revenue collection was affected by poor billing system, high level of malfunctioning meters, high rate of non-revenue water and low confidence of customers with their service provider.

Costs for operation and maintenance (O&M) and revenue collection

O&M and revenue collection for water supply

At the time of the study, Chiredzi town council was facing financial problems, especially for upgrading the system. For example, water supply system cannot supply water to the users for 24 h because their storage tanks need upgrading to meet the daily requirement. The council was also unable to pay its staff because of financial problems, which is de-motivating them. Table 3 shows that total O&M costs for water supply declined from USD 455,469 in 2010 to USD 322,621 per annum in 2014. The decrease in costs was caused by retrenchment, which started in 2012 up to 2013. However, it was noted that although there was a decline in costs, the costs were higher than the revenue collected from 2010 up to 2013. The study found out that only in year 2014 the collected revenue was higher than the costs incurred for that year. It was worth noting that in 2010 there was an outbreak of cholera and high costs (USD 455,469) were incurred for purchasing water treatment chemicals. The average collection ratio was found to be 46% meaning that the revenue collected was less than the expected in general, except for 2014. The scheme was not operating viably from 2010 up to 2013, and in 2014 it started to accrue marginal surplus that could be used for system upgrading and contingency measures such as breakdowns.

Table 3 shows that the O&M cost for wastewater management were higher than collected revenue as from 2010 up to 2011 and thereafter the collected revenue were higher than the cost incurred. The major O&M activities were noted to be regular staff, repairs/maintenance costs and other costs. It was noted that although the costs were less than revenue collected, their differences were marginal, especially in the year 2012 where the costs were USD 100,153 compared to USD 110,765 revenue collected. The study findings revealed that as from 2010 to 2014 the expected revenue ranged from USD 240,567 to USD 295,047 per annum. The collection ratio was found to be 47%, and this reflects that the revenue collected for the given period was less than the expected revenue.

It was observed that amount of revenue collected by the service provider was lower than the costs incurred from years 2010 to 2012. This reflects that the council had no surplus funds for expansion and maintenance, meaning that the systems were run unsustainably. From the key informant interview with the financial department, the losses which the council suffered from 2010 up to 2012 were attributed to the cholera outbreak of 2010 and political campaigns of 2011/12 elections. Minister of
Sustainability index for water and wastewater systems

Sustainability of water and wastewater systems depend on numerous factors including legal, policies and institutional framework, community participation and social aspects, economic factors, financing and cost recovery, technical aspects, capacity building and natural environment (Mays, 2006; Gowda and Doddaswamy, 2011; Juwana et al., 2012). Various researches done in sub-Saharan Africa on sustainability of community water projects have studied at least two of these factors (Marcus and Onjala, 2008; Spaling et al., 2014; Kwangware et al., 2014). However, Peter and Nkambule (2012) concluded that technical and social factors were more important than other factors. Others have measured key determinants of sustainability such as technical, financial, social and environmental factors (De Carvalho, 2007; Spaling et al., 2014), an approach that was adopted in this study.

Table 3. Water supply financial requirement for O&M and revenue collected.

<table>
<thead>
<tr>
<th>Financial year</th>
<th>2010</th>
<th>2011</th>
<th>2012</th>
<th>2013</th>
<th>2014</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expenditure component</td>
<td>A: Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total O&amp;M cost (USD)</td>
<td>455,469</td>
<td>444,730</td>
<td>424,598</td>
<td>317,221</td>
<td>322,621</td>
</tr>
<tr>
<td>Revenue collected (USD)</td>
<td>325,069</td>
<td>420,789</td>
<td>300,290</td>
<td>311,151</td>
<td>478,693</td>
</tr>
<tr>
<td>Expected revenue</td>
<td>675,567</td>
<td>738,330</td>
<td>738,330</td>
<td>850,678</td>
<td>982,047</td>
</tr>
<tr>
<td>B: Wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total O&amp;M cost (USD)</td>
<td>109,613</td>
<td>106,648</td>
<td>100,153</td>
<td>101,715</td>
<td>103,485</td>
</tr>
<tr>
<td>Revenue collected (USD)</td>
<td>90,450</td>
<td>102,679</td>
<td>110,765</td>
<td>174,687</td>
<td>154,584</td>
</tr>
<tr>
<td>Expected revenue</td>
<td>240,567</td>
<td>240,567</td>
<td>245,373</td>
<td>295,047</td>
<td>295,047</td>
</tr>
<tr>
<td>C: Water and wastewater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total revenue collected (USD)</td>
<td>415,519</td>
<td>505,468</td>
<td>411,055</td>
<td>485,838</td>
<td>633,277</td>
</tr>
<tr>
<td>Total O&amp;M cost (USD)</td>
<td>565,082</td>
<td>551,378</td>
<td>524,751</td>
<td>418,936</td>
<td>426,106</td>
</tr>
<tr>
<td>Surplus/Shortfall (USD)</td>
<td>(149,563)</td>
<td>(45,910)</td>
<td>(113,696)</td>
<td>66,907</td>
<td>207,117</td>
</tr>
</tbody>
</table>

Financial aspect

The results indicated that the financial determinant had an average score of 5.8 and was the second last among the sustainability determinants studied (Table 5). The indicator, capacity to pay for the services scored the lowest of 5.25. This was mostly affected by the variable collection efficiency which had a score of 1. It was worth noting that collection efficiency of sufficient revenue was greatly dependent on the consumer’s satisfaction level to the quality of services they receive as mentioned by Bhandari and Grant (2007). A household questionnaire was used to assess the willingness to pay and 93% of the respondents were willing to pay, but only 65% paid their bills. From this study, it was observed that the town council should improve on tariff collection efficiency by improving the quality of service delivery. It was also noted that 45% of the respondents are not employed, but they depend on informal business, thus their incomes are low and irregulars, meaning that they cannot afford to pay for the bills when due. Their incomes range from 100USD to 200USD which is far below poverty datum line of 450
USD (Zimstat, 2012). Non-revenue water was 65%, reflecting that only 35% of the generated water was billed. It was noted that high level of unaccounted for water was impacting negatively on the financial status of the service provider.

Financial aspect have low index of 5.8 indicating slow progress towards sustainability. It was observed that %NRW, collection efficiency and unemployment rate with scores of 3.8, 1.0 and 4.5, respectively were the major sub-indicators, which brings down the financial aspect index. These indicators had a huge impact on cost recovery and capacity of users to pay for services. It is worth noting that cost recovery is linked to technical aspect sub-indicators such as metering level, unaccounted for water and leakage detection system. Therefore, by improving on leakages detection, sorting out malfunctioning meters and reduction of unaccounted for water, cost recovery is improved.

Stakeholder participation is generally low, which has led to low percentage of users actually paying for the services, thus poor sustainability of water supply and wastewater systems. There is poor dissemination of information from management to stakeholders as evidenced by no interruption notification for services. The water users association was also found to be effective in terms of improving service delivery and if sustainable management of water supply and wastewater systems is to be achieved. This is because water users association gives the insight of services delivery levels that are on ground.

Social aspect

Among the social sustainability indices, the level of information dissemination had the lowest score of 0.4. A household questionnaire was used to assess the level of information dissemination and 96% of the respondents mentioned that they have never been informed of interruptions or development of services systems. Thus, users need to be informed of interruptions and any activities involving the development of services systems. It was also noted that the level of stakeholder participation (56%) is very low. This findings showed that the service provider is not involving users in the development and activities of water supply and sanitation systems. About 78% of the respondents were satisfied by water quality and service tariffs. High consumer

---

**Table 4. Technical aspect sustainability scores (Aspect weight = 25%).**

<table>
<thead>
<tr>
<th>No.</th>
<th>Indicators</th>
<th>Variable</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Service coverage</td>
<td>Population served</td>
<td>7.8</td>
</tr>
<tr>
<td>2</td>
<td>Service coverage</td>
<td>Water supply coverage</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>Service coverage</td>
<td>Sewage network coverage</td>
<td>7.3</td>
</tr>
<tr>
<td>4</td>
<td>Water production and consumption</td>
<td>Quantity produced/d</td>
<td>7.2</td>
</tr>
<tr>
<td>5</td>
<td>Water production and consumption</td>
<td>Per capita requirement/d</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Water losses</td>
<td>Metering level</td>
<td>2.0</td>
</tr>
<tr>
<td>7</td>
<td>Water losses</td>
<td>Unaccounted for water</td>
<td>4.0</td>
</tr>
<tr>
<td>8</td>
<td>Water losses</td>
<td>Leakage detection system</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total average score</td>
<td>6.2</td>
</tr>
</tbody>
</table>

**Table 5. Financial aspect sustainability score (Aspect weight = 25%).**

<table>
<thead>
<tr>
<th>No.</th>
<th>Indicator</th>
<th>Sub-indicator</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cost recovery</td>
<td>% users paying for water and sewage</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>Cost recovery</td>
<td>% Non-Revenue Water (NRW)</td>
<td>3.8</td>
</tr>
<tr>
<td>3</td>
<td>Cost recovery</td>
<td>% willingness to pay</td>
<td>9.3</td>
</tr>
<tr>
<td>4</td>
<td>Capacity to pay for the services</td>
<td>Average Income levels</td>
<td>5.5</td>
</tr>
<tr>
<td>5</td>
<td>Capacity to pay for the services</td>
<td>Unemployment rate</td>
<td>4.5</td>
</tr>
<tr>
<td>6</td>
<td>Capacity to pay for the services</td>
<td>Collection efficiency</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td>Capacity to pay for the services</td>
<td>Average tariffs level</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total average score</td>
<td>5.8</td>
</tr>
</tbody>
</table>
satisfaction is a good indicator of sustainability management for both water supply and sanitation systems. The results agreed with those of Kwangware et al. (2014) who mentioned that the level of consumer satisfaction is one of the factors that influence their willingness to pay for the services. Table 6 shows that the overall average social score was 5.6. From the results, level of information dissemination, response time to complaints and continuity of water supply which had scores of 0.4, 3.3 and 3, respectively were the sub-indicators which brings down the social index. These three sub-indicators can be improved through education and awareness and upgrading the system to meet daily demands.

Environmental aspect

Sub-indicators of environmental sustainability include the quality of wastewater effluent, management of faecal sludge and compliance of wastewater treatment with Environmental Management Authority (EMA) policy. Others include water quality monitoring and reuse of domestic water after consumption. From the key informant interview and water and wastewater analysis, it was observed that the service provider complied with National Environmental Protection standards of 2007. It was noted, during physical inspection of the systems that faecal sludge matter was composed for 6 months before using it as manure. Sludge from the settling tanks was disposed in drying beds and water was allowed to drain through the unearthed channel to Mteri Dam where it is used for sugarcane irrigation. From field observation, effluent reuse is only practiced by the residents who have gardens around the stabilizing ponds for irrigation of tomatoes, vegetables, sesame, okra and maize, but root crops such as carrots have been avoided. For those who are into informal business, they sell these crops to raise household income. The council is not recycling water at all; instead it leaves the wastewater to flow to Chiredzi River. The overall average environmental score of 7.3 was the highest of all the four determinants under study, which reflects high sustainability (Table 7). However, sustainability index of environmental aspects can be raised by implementing water reuse for irrigation and aquaculture. It is worth mentioning that in emerging rapidly urbanising developing countries, sharp increase in demand for water is expected due to demands for irrigation and industry. The expansion of irrigated crop areas using recycled water may be a feasible option because of competition for water between economic sectors (Jägermeyr et al., 2016).

Overall sustainability index

Each of the determining factors, namely technical, financial, social and environmental aspects contributed 25% to the overall sustainability index. The environmental determinant had the highest sustainability index of 7.3, followed by technical, financial and social aspects with scores of 6.2, 5.8 and 5.6, respectively. The composite sustainability index was found to be 6.2 on a 10-point scale. This indicates that the performance of water supply and wastewater management is considered to be satisfactory progress towards sustainability in accordance with De Carvalho (2007). However, there is a need for improvement on financial, technical and social aspect. Other areas of improvement include reuse of water and wastewater, water metering and auditing should be implemented to minimize water losses.

CONCLUSIONS AND RECOMMENDATIONS

From the results of this study, it can be concluded that Chiredzi town is lagging behind in terms of service coverage, with 77.9 and 72% for water and sewerage systems, respectively. This was contributed by the failure of council to expand and upgrade the old and worn out
infrastructure. It was further observed that issues of tariff settings, punishment of defaulters and institutional arrangement for regulation of water management in the urban areas are not adequately addressed in the Water Policies and Acts of Zimbabwe. In absence of proper institutional arrangement, Chiredzi town has failed to raise funds for rehabilitation, expansion and upgrading of water supply and wastewater system. A composite sustainability index of 6.2 out of 10, suggests that sustainability of Chiredzi town water supply and wastewater system was satisfactory progress towards sustainability. However, improvements are required in some areas including reuse of wastewater, increasing operating water meters and minimization of water losses, which are currently 20 and 65%, respectively. In general, the stakeholder participation is generally low and this has consequently contributed to low percentage of users actually paying for the services, thus poor sustainability of water supply and wastewater systems. To improve on water supply and sanitation service delivery, the Government of Zimbabwe has to ensure the budget for Urban Councils includes small town such as Chiredzi, so that they keep on operating despite revenue collection being low. To improve on the sustainability index, service providers must increase revenue collection, ensure reduction of non-revenue water, recycle and reuse treated wastewater, reduce service interruptions and improve stakeholder participation through awareness and sensitization programs to users.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ACKNOWLEDGEMENTS

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Table 7. Environmental sustainability score (Aspect weight = 25%).

<table>
<thead>
<tr>
<th>No.</th>
<th>Indicator</th>
<th>Sub-indicators</th>
<th>Score</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Wastewater management</td>
<td>Effluent quality</td>
<td>8.3</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Disposal of faecal sludge</td>
<td>8.9</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Compliance with EMA policy</td>
<td>8.8</td>
</tr>
<tr>
<td>4</td>
<td>Domestic water management</td>
<td>Water quality monitoring</td>
<td>8.5</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>Water reuse</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Sludge disposal</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>Total average score</td>
<td></td>
<td>7.3</td>
</tr>
</tbody>
</table>


United Nations Children’s Fund (UNICEF) and World Health Organization (WHO) Joint Monitoring Programme (JMP) for water supply and sanitation (2017). Progress on drinking water and sanitation and hygiene 2017, Updates and SDGs baselines, New York, USA.


Exploratory study of Polycyclic Aromatic Hydrocarbon (PAH) contributions to household air pollution arising from improved cookstove use in rural Malawi

Kondwani R. Chidziwisano\(^1\), Michael O. Rivett\(^1\), Amornphat Tadsanaprasittipol\(^1,3\), Laura A. McGregor\(^1,4\) and Robert M. Kalin\(^1\)

\(^1\)Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, UK.
\(^2\)Department of Environmental Health and WASHTED, Polytechnic, University of Malawi, Blantyre, Malawi.
\(^3\)Pollution Control Department, 92 Soi Phahon Yothin 7, Phahon Yothin Road, Phayahtai District, Bangkok 10400, Thailand.
\(^4\)SepSolve Analytical Ltd, 22 Commerce Road, Lynchwood, Peterborough, Cambridgeshire, PE2 6LR, UK.

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Around three million premature deaths annually are ascribed to household air pollution (HAP) arising from inefficient burning of biomass and emissions of products of incomplete combustion. The developing-world response has been widespread adoption of improved cookstove (ICS) technologies. This exploratory study evaluates variation in polycyclic aromatic hydrocarbon (PAH) attached to inhalable particulate matter (PM) in rural Malawi households adopting ICS use. PM literature supports HAP exposure to inhalable PM is lowered, albeit variably, compared to traditional fires, but remains significant. Similar is expected for PAH; however, datasets lack discerning PAH chemical-specific contributions to risks. The study introduces the Malawian context, invokes a PAH reconnaissance approach sampling kitchen soot ‘spots’ and residential dusts, and relates PAH occurrence to the two sample types collected and ICS types surveyed. The total PAH for dusts was low (c. 2 \(\mu g/g\) mean), with volatile 2-ring naphthalene dominant. Soot total PAH was much higher (c. 200 \(\mu g/g\) mean to a maximum of 815 \(\mu g/g\)). Soot from PM emissions poses a major primary health concern. Despite PAH trends not being obvious with ICS type (limited sample size) and the wide range in soot total PAH, soot PAH-fingerprints were well constrained with low variation of diagnostic PAH ratios, exhibiting n-ring fingerprints close to the soot median (0.1% 2-ring, 20% 3-ring, 61% 4-ring, 14% 5-ring, 5% 6-ring PAH). These corroborate the expected wood-related combustions sources, but also point to the needs to understand factors that control wide variations in PM and (total) PAH emitted as these control variations in HAP and differing risks posed to individual households. Further household-based research is thus recommended discerning relationships between PM emissions and PAH contents, driving the chemical-composition health risks. These should establish influences on PAH exposure arising from ICS type/model selected, operational modes, building/ventilation conditions, variable fuel sources and non-optimal ICS use.

Key words: Improved cookstoves (ICS), polycyclic aromatic hydrocarbon (PAH), household air pollution (HAP), particulate matter (PM), Malawi, indoor air pollution (IAP).
INTRODUCTION

Nearly three billion people rely on the burning of biomass for their everyday cooking and heating (IEA, 2017). In the rural developing world, especially Sub-Saharan Africa, 80% use wood, charcoal, animal dung and crop residue biomass fuels within simple ‘three stone fires’ (TSF) or traditional stoves (Foell et al., 2011). Although biomass use is not unsound as such, unsustainable harvesting and deforestation, alongside inefficient dirty energy-conversion practices has caused unprecedented health impacts (Foell et al., 2011; Wathore et al., 2017). A staggering 2.8 million premature deaths each year, mostly women and children, is ascribed to household air pollution (HAP) (indoor air pollution (IAP)) due to inefficient burning of biomass and emission products of incomplete combustion (PIC) (IEA, 2017). The World Health Organization (WHO) estimate even higher, attributing nearly 4 million premature deaths to illness associated with HAP due to poor cooking practices (WHO, 2018).

Documented health effects include acute respiratory infections, chronic obstructive pulmonary disease, pulmonary tuberculosis, perinatal and infant mortality and various cancers (Gall et al., 2011; WHO, 2018). PIC include CO, CH₄, polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM) that includes black carbon, ‘soot’, aerosols (Wathore et al., 2017). Our research concerns risks posed by particle-bound PAH transported on inhalable PM, a long recognised exposure pathway to biomass stove users (Gachanja and Worsfold, 1993; Lawal, 2017; Ramdahl, 1985; Saksena et al., 1992). PM-bound PAH poses significant health concern as 50-75% of emitted particulates are of inhalable size, with greater PAH mass adsorbed to fine soots (Gachanja and Worsfold, 1993; IARC, 2013). Despite its low per capita energy consumption, Africa’s per capita PAH emissions are amongst the highest globally due to the high proportion of residential/commercial biomass burning (Shen et al., 2013a). Some 63% of total PAH emissions globally occur within the residential/commercial sector, reaching 67-80% in Africa (Shen et al., 2013b).

Growing use of improved cookstoves (ICS) forms the cornerstone response globally (Grieshop et al., 2011; Thomas et al., 2015; Wathore et al., 2017). ICS sophistication ranges from rudimentary stoves using local materials, up to state-of-the-art forced-draft cookstoves (FDCS) with electric fans (Grieshop et al., 2011; Jetter et al., 2012; Thomas et al., 2015; Wathore et al., 2017). ICS uptake is rapidly growing due to Sustainable Development Goal agenda to reduce air pollution-related disease burden under SDG 3, and to ensure access to clean fuel energy technology under SDG 7. Concerns remain however. Thomas et al. (2015) conclude from their review of 36 studies globally, that despite ICS interventions reducing exposure to HAP, pollutant levels are unlikely to meet WHO recommendations. Laboratory bench-testing indicates ICS performance in reducing HAP varies over two orders of magnitude (Grieshop et al., 2011) and often over-estimates household performance, by 2-5 times for PM emissions (Rodent et al., 2009; Shen et al., 2013b) where non-ideal user operation may prove a significant issue (as confirmed in Malawi by Wathore et al. (2017)). Even best performing ICS (FDCS) under controlled Malawian field-test kitchens still resulted in PM₂.₅ (< 2.5 μm ‘fine particle’) emissions 22% of TSF levels, with others much worse (Jagger et al., 2017). Continuing, variable emissions, alongside less-than-expected health benefits, endorse the need for studies that examine underlying chemical-composition influence (Mortimer et al., 2017; Romieu et al., 2009).

Significant rationale exist to evaluate PAH exposure risks associated with ICS use and chemical toxicity of the complex PAH fingerprint transported on PM (Brook et al., 2010; Keshtkar and Ashbaugh, 2007; Lawal, 2017; Taylor and Nakai, 2012). Fingerprint characterisation is important due to varying individual PAH toxicity and resultant variable chronic exposure risks arising from the carcinogenicity and mutagenicity, especially of higher ring PAH (IARC, 2013). As more volatile 2- to 3-ring PAH are released into the gas phase (Vineis et al., 2004; Brook et al., 2010), attention is more towards very low volatility 5- and 6-ring PAH preferentially associated with ultrafine PM (< 0.1 μm), and moderate volatility 3- and 4-ring PAH predominant in larger particles (Keshtkar and Ashbaugh, 2007). It should be further recognised that the burden of illness due to PAH exposure may be greater than currently estimated from carcinogenicity and cardiovascular morbidity, as respiratory conditions may be significant (Cakmak et al., 2017). Furthermore, PAH are immunosuppressive (White Jr., 2008) with various disease outcomes linked to acute exposure including inflammation of the eye, skin, and respiratory and prenatal exposure associated with, for instance, fetal growth restriction and childhood asthma (Ferguson et al., 2011) and heightened health risks to communities with increased rates of AIDS (acquired immunodeficiency syndrome). Understanding PAH emission sensitivity to ICS design and user operation requires in-household PAH datasets covering a range of ICS design type and use conditions. Lack of data is ascribed to the demands of implementing PAH analysis in developing countries, and primary use of PM and CO to regulate HAP human exposure with PAH risks then being inferred. Of the intervention studies reviewed by Thomas et al. (2015),
only the Mexican study of Riojas-Rodriguez et al. (2011) had pollutant outcomes relating to PAH.

Our aim is to undertake an exploratory study of the variation in PAH emissions associated with ICS use within rural Malawian households thereby permitting preliminary evaluation of potential residential occupant exposure to PAH risks via inhalable PM. Objectives were to: review the context of ICS use in Malawi; adopt a simple sampling approach that allowed convenient reconnaissance of PAH occurrence in ICS user households; to measure total and individual PAH to establish PAH fingerprint characteristics and any relationships to the various ICS or sample types evaluated; and, provide forward recommendations on household study research.

MATERIALS AND METHODS

Study setting and review

Rural Malawians are among the poorest of the global poor. Malawi is a low-income country, ranking 170 out of 188 in the 2015 Human Development Index (World Food Program, 2018). It continues to receive significant international aid facilitating its quest to meet a host of SDGs. Current population is 18 million, growing by 2.9% per annum (World Bank, 2018), with the majority rural (c. 85%). Most rural inhabitants of the Chikwawa District studied in semi-arid Southern Malawi are subsistence farmers. They live on less than $0.50 (USD) a day with a mean, but increasing, life expectancy of just 45 years (Water for People, 2017). Water, food and energy security is low. Just 2% of Malawian households are estimated to cook with electricity and many are daily exposed to HAP from open fires. In 2010, 99.5% of the rural Malawians and 85% of the urban population were using solid fuels, mostly within TSF for cooking (Malawi-Government, 2010). Biomass fuel will likely remain the most reliable household source of cooking energy in semi urban and rural Malawi due to its accessibility.

Malawi targets adoption of ICS in two million homes, some 65% of its households, by 2020 (Jagger and Jumbe, 2016). The programme is inextricably linked with the plight of Malawi’s forests, depleting at 2.8% per annum due to illegal logging by communities (Gercama and Bertrams, 2017). Gercama and Bertrams (2017) report on the progress indicated by the National Cook Stove Steering Committee (a coordinating body of officials, NGOs, etc.), that half-a-million ‘clean and efficient’ cookstoves are now in use. Illegal logging is attributed to surging charcoal demand in Malawi’s cities. According to the government, 54% of urban women now use the ‘black gold’ for cooking, recognising it cleaner and quicker burn than firewood with use considered a status symbol (Gercama and Bertrams, 2017). Unless sustainably sourced, charcoal production and sale is banned; however, only one commercial licence for production has been issued. Quoting Gercama and Bertrams (2017), “the illegal trade is booming, serviced by rural residents who scrape a living turning timber into charcoal in a highly inefficient process which wastes enormous amounts of wood”.

The above is indicative of the Malawian climate in which ICS research and development finds itself. Cookstoves are foremost in Malawian policy agenda, cutting across energy, environment, health, and gender sectors (Jagger et al., 2017). ICS implementation is supported by a growing diversity of cookstove research in Malawi, including: Wathore et al. (2017) evaluating the impacts of traditional, natural- and forced-draft cookstoves, and Piddock et al. (2014) on periurban domestic biomass use; Fullerton et al. (2011) on wood smoke impaired lung function, Fullerton et al. (2009) on biomass fuel emissions and respirable dust, and Mortimer et al. (2017) confirming interventions failed to prevent pneumonia; Timko et al. (2016) on tree species preference and Fisher and Shively (2005) on forest use; O’Shaughnessy et al. (2014) on an electricity-producing portable ICS, Orr et al. (2015) on integrated food-energy systems; Jagger and Jumbe (2016) on household willingness to adopt ICS and Cundale et al. (2017) on household costs and benefits; Das et al. (2017) on health outcomes for women; and Jagger et al. (2017) on controlled field testing of TSF and ICS and up-scaling ICS programmes. None of these studies directly focuses upon PAH and hence our research is viewed complimentary.

Field survey of households: dust and soot sampling

Our exploratory study on PAH emissions from ICS use was afforded as an opportunity implemented alongside other (unrelated) health-based research in Malawi that facilitated field survey household access. Field collection of household kitchen soot and residential dust samples for PAH analysis was undertaken from randomly selected traditional households equipped with ICS located in Balaka District and Chikwawa District of rural semi-arid Southern Malawi (Figure 1). Households typically comprised mud walls, dirt floors, small wooden windows and doors with grass-thatched roofs. Structural conditions are characterised by poor ventilation, including smoke generated from cooking. Although these areas support both indigenous and exotic trees, including bush species that are used for fuel, scarcity of fuel wood has led to some community members using any combustible material such as animal dung, crop residues and even plastic materials. Subsistence agriculture provides the predominant source of income with open burning of crop residues common practice posing greater PAH risks to the male population.
Automobile use is limited and exposure to related-PAH emissions not common.

Residential dust samples were obtained via careful collection of indoor or sweeping from 38 households in Chikwawa District (Chidziwisano, 2012). Samples are expected to include coarse particle sizes generated during combustion that are rapidly deposited due to their relatively high mass. They provide a readily collected (for exploratory study) aggregate sample of deposited PM of varying size fraction associated with the ambient air and may contain PAH originating from a variety of sources – not only from fire or cooking stove origins, but, say, environmental tobacco smoke, or PM entry to households from field burning, vehicle or machinery emissions. Recent quantification of 24 h average elevated total inhalable dust concentrations of 268 µg m$^{-2}$ and 185 µg m$^{-3}$ in rural Chikwawa and urban Blantyre (Fullerton et al., 2009) underscored requirements to evaluate PAH exposure associated with dust inhalation.

Soot samples, again a readily available sample type, were collected from the inside walls of domestic kitchens where soot ‘spots’ had accumulated. Samples were obtained by scrubbing with a clean brush and anticipated to contain fine-particle size ranges from combustion particulate matter that becomes dispersed and suspended in the household to eventually deposit on inside walls. Fifteen households in Balaka were randomly selected where ICS were in daily use (Chidziwisano, 2012). Five ICS brands (types) of differing designs were investigated including the PCI mud stove (at 5 household sites), Chitezto Mbaula (7 sites), Briquette (1 site), Aleva (1 site) and Esperanza stove (1 site) (Chidziwisano, 2012). Achieving similar coverage of each ICS type was not possible at the time of this exploratory study due to the uptake of ICS being emergent and quite limited. Most ICS in use were generally simple to construct with NGOs providing training. The Chitezto Mbaula stove is the only portable design; this could ideally be used outside, or the most ventilated area of a residence, to minimise indoor smoke. The Aleva and PCI mud stoves are built using compacted soil and mud respectively; they hence circumvent problems in locally sourcing clay required for some ICS. The Esperanza stove is a larger and more expensive ICS with ceramic-lined air and combustion chambers; it is perceived, due to its expense, less popular. The exploratory study nature did not allow opportunity to evaluate factors such as type (and seasonality) of fuel burnt, nor influential design features of the residence (kitchen size, ventilation, etc.).

Dust and soot samples were kept in tightly capped glass vials then transferred to the University of Strathclyde laboratory in Scotland where they were stored at -80°C until extraction and analysis. PAH analysis facilities were not available in Malawi.

### Laboratory extraction of PAH

A growing wealth of methods exists for environmental sample PAH analysis (Lawal, 2017). Samples were analysed within our programme of wider research developing analytical methods for the analysis of PM-bound PAHs (Tadsanaprasittipol, 2016), developing rapid extraction and analysis of the 16 US EPA priority PAHs (Chidziwisano et al., 2003; US EPA, 1999). The detail of Tadsanaprasittipol’s (2016) method development (mostly completed in urban Thailand with supporting work in rural Malawi) was not provided, but a key outcome was the accelerated solvent extraction (ASE) method developed and used herein. It is a highly efficient extraction technique for particulate-bound PAH with a sample extraction time of 30 min, significantly less than conventional Soxhlet extraction.

Solvents used (n-hexane, dichloromethane, toluene) were of analytical grade (Fisher Scientific, Loughborough, UK). All PAHs and deuterated PAHs were purchased from Sigma–Aldrich (Gillingham, UK). Anhydrous sodium sulphate, silica gel 60 and diatomaceous earth were activated for 8 h at 450°C prior to use.

Silica gel 60 was then deactivated by 10% water (w/w). Extraction of target analytes was performed using an accelerated solvent extraction system (ASE 350, Dionex, Camberley, UK) equipped with 34 ml extraction cells. Soot sample extractions were performed at 150°C with a heating time of 7 min and using 3 cycles with a static time of 6 min. The solvent used for all extractions was a mixture of hexane and toluene (4:1 v/v). A flush-volume of 60% cell volume and purge time of 60 s was used. Dust sample were extracted at 110°C, otherwise conditions were similar to soot sample extraction. Deuterated surrogates (D8-naphthalene, D10-fluorene, D10-fluoranthene and D12-chrysene prepared as a 500 µg/ml stock solution in dichloromethane) were added to each sample to monitor extraction efficiency. ASE extraction cells were prepared by lining the lower lid with two filter papers to collect unwanted particulates, then filling the cell with 3 g of silica gel/sodium sulphate (4:1 ratio w/w). A portion of soot sample (approximately 5 g) was then added and the remaining cell volume was packed with diatomaceous earth (inert filtration agent). A Büchi SynCore Analyt (Oldham, UK) was used to concentrate the sample extracts to approximately 1 ml. The final sample volume was adjusted to 1.5 ml and spiked with internal standards for subsequent analysis. All extracts were spiked with 60 µl of internal standard (550 µg/ml stock solution of D10-fluoranthene in dichloromethane) prior to analysis and stored at -80°C between analyses.

### GC-MS analysis of PAH

A Thermo Scientific (Hertfordshire, UK) Trace Ultra GC equipped with a DSQII quadrupole mass spectrometer and Triplus autosampler was used for all GC-MS analyses. Helium (BOC Ltd., 99.999% purity) was used as the carrier gas at a flow rate of 1 ml min$^{-1}$. A J&W Scientific DB-5MS column with dimensions 30 m × 0.25 mm i.d. × 0.25 µm film thickness was used for all GC-MS analyses. The injector temperature was set at 230°C, with 1 µl of each soot sample extract was injected at a split ratio of 1:10. All standards and extracts were analysed with the oven temperature programmed at 55°C with 2 min isothermal, then increased at 10°C min$^{-1}$ to 110°C, increased at 3°C min$^{-1}$ to 210°C, then at 8°C min$^{-1}$ to 320°C (maintained for 15 min), with a transfer line temperature of 350°C. The MS was operated in full scan mode using an ion source temperature of 200°C. Dust sample extracts were analysed using splitless mode at the inlet temperature of 230°C. Helium carrier gas was set at 1 ml min$^{-1}$. All standards and extracts were analysed with the oven temperature programme at 60°C with 3 min isothermal then increased at the rate of 5°C min$^{-1}$ to 310°C (maintained for 1.5 min). The MS was operated in full scan mode with the mass range of 50-650 µ in the scan rate of 500 µ s$^{-1}$. The ion source temperature was 220°C.

Target PAHs in the soot and dust extracts were quantified by GC-MS using a calibration series containing 16 of the US EPA priority pollutant PAHs. The following PAHs were quantified: naphthalene (N), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz[a,h]anthracene (DBA), indeno[1,2,3-cd]pyrene (IP), and benzo[g,h,i]perylen (BP). All samples and standards were analysed in triplicate.

Figure 2 shows a box plot of recovery percentages of surrogate deuterated PAH (d-PAH) spiked onto dust samples collected from the 38 households. The surrogate D-PAHs adsorbed by dust particles were demonstrated to be extracted at high recoveries, for both the 2-ring and 4-ring PAH shown. The mean recovery of naphthalene-d8 was 85% ± 18% and that of chrysene-d12 higher at 89 ± 16%. The ASE extraction method hence gave very satisfactory results for dust samples. The shown efficient extraction of deuterated surrogate concentrations is within the US EPA.
Data processing and chemometrics

As the samples contained a range of compounds outside of the 16 quantified PAHs, the peak areas of a variety of compounds were also compiled for each sample (normalised to the peak area of internal standard) and compared statistically. These include methoxyphenol and sulphur-containing compounds.

Matlab statistical software (version R2011a, Mathworks Inc.) was used for principal component analysis (PCA) of the two datasets. Principal component analysis is a multivariate statistical technique that allows the simplification of complex datasets into principal components (PCs) which account for the majority of the total variance (Meglen, 1992). The sample score determine the position of each sample in the two-dimensional plot. Samples that are more similar show alike scores on each PC. The loadings can also be examined to show the contribution of each variable (PAH in this case) towards the formation of each principal component.

RESULTS

PAH in dust samples

PAH in dust samples from 38 households, shown in order of increasing total PAH concentration (Figure 3a), ranged from 0.37-7.07 μg/g total PAH (16 US EPA priority). Individual PAH concentrations ranged from below detection limits (0.002 to 0.005 μg/g across the various PAH) up to 6.52 μg/g. Naphthalene (N), the lowest molecular weight and most volatile PAH, accounted for this dataset maximum concentration and the maximum individual PAH concentration within all dust samples. N dominance is evident in the PAH fingerprint composition resolved within the individual sample plotted bars (Figure 3a).

Dominance of 2-ring PAH arising from N presence is obvious in Figure 3b. Whilst some 3-ring PAH, and to a lesser extent 4-ring PAH, are present in the dust samples; their concentrations remain low. Concentrations of 5-ring and 6-ring PAH were below, or barely exceeded, detection limits. Examination of the relative proportion of the various ring PAH (Figure 3c) reveals that greater mass proportions of the higher ring categories are found in some, but not all, samples with lower total PAH concentrations around 1 μg/g where 2-ring mass proportions decline to around 35-55%. Otherwise, 2-ring proportions typically account for around 65-90% of the dust PAH mass. Dust sample PAH associated with this coarse particle size range is hence dominated by the low molecular weight, most volatile PAH fraction. With one marginal exception, total PAH of dusts samples were below 5 μg/g.

PAH in soot samples

Soot samples from 15 households are shown in Figure 4a ordered in cookstove type, and then with each type, by increasing total PAH. Concentrations spanned two orders of magnitude from 13.7 to 815 μg/g total PAH. Marked variation of total PAH within individual cookstove types is apparent where multiple samples were available for comparison. For example, the total PAH for PCI cookstoves (n = 5) varies from 52-226 μg/g, with no samples exhibiting similar values. For Chitetezo cookstoves (n = 7), total PAH is also quite dissimilar across samples that range from the soot minimum of 13.7 up to 678 μg/g. Individual PAH concentrations were mostly above detection limits leading to a complex and varied PAH fingerprint composition being apparent across the dataset shown by the sample fingerprint detail (Figure 4a). Highest individual PAH concentrations detected were in the c. 100-250 μg/g range; these occurred for 3-ring phenanthrene (PHE) up to a maximum of 117 μg/g, for 4-ring fluoranthene (FLT) up to 217 μg/g, and 4-ring pyrene (PYR) up to 217 μg/g.
Figure 3. Dust samples (n=38) ordered with increasing total PAH concentration: (a) individual PAH composition; (b) concentration composition classified by number of rings in molecule; (c) mass proportion of total PAH mass classified by number of rings.

Dominance of the 4-ring PAH composition within the soot PAH mass is clearly shown in Figure 4b. Lesser contributions from 3-ring, with more minor contribution of 5-ring PAH, and trace contributions from 6-ring PAH are
Figure 4. ICS soot samples (n=15) grouped by ICS type and increasing total PAH within that group: (a) individual PAH composition; (b) concentration composition classified by number of rings in molecule; (c) mass proportion of total PAH mass classified by number of rings.

discernible across the soot dataset. Examination of the relative proportion of the various ring PAH within the soot (Figure 4c) indicates the relative proportion of the various ring PAHs remains quite similar across the soot dataset,
Figure 5. Box (25th and 75th percentile) and whisker (5th and 95th percentile) plots of individual and total PAH concentrations in: (a) dust samples; (b) ICS samples.

Comparison of dust and soot PAH

PAH concentrations associated with kitchen soot are consistently much higher than the household dust as illustrated in Figure 5 comparative box plots (note the differing (log) concentration scales). Total PAH for the dust exhibit an average and median of 2.22 and 2.06 μg/g respectively. These compare to soot values of 270 and 193 μg/g, around two orders of magnitude higher. 2-Ring naphthalene (N) of average and median concentration in the dust of respectively 1.80 μg/g and 1.68 μg/g and range 0.16-6.52 μg/g dominates the dust PAH content. N concentrations are similar across the soots sampled, but lower, at average and median concentrations of 1.4 μg/g and 0.5 μg/g respectively, with a range of <0.1-4.4 μg/g. Contrasting with the dusts, the
median contribution of 2-ring N to the total PAH soot mass is negligible at 0.1%.

Excluding N, all other individual PAH with detectable concentrations in the dust occur almost exclusively in the range 0.01- 0.1 μg/g (Figure 5a). Exceptions to this are for 3-ring PHE with a median of 0.11 μg/g and maximum of 0.32 μg/g and a few concentrations of 3-ring ACY and 4-ring FLT and PYR that just exceed 0.1 μg/g. Interestingly, three of these PAH (PHE, FLT and PYR) are the aforementioned individual PAH maxima encountered in the soot samples. Their more elevated occurrence within the soot compared to other PAH is illustrated in Fig. 5b; median concentrations at 26.8 μg/g PHE, 43.4 μg/g FLT and 49.5 μg/g PYR compared to soot medians for all other PAH spanning 0.5- 13.3 μg/g with an overall median of those PAH around an order of magnitude lower at 4.5 μg/g. It is surmised from the similarity of the 3-ring and 4-ring PAH higher concentration fingerprint between the dust and soot, that some soot particles are quite likely deposited and incorporated within the household dust sampled and may account for this similarity.

Comparison of dust and soot samples by n-ring classification illustrates the dominance of the 2-ring concentration mass in the dust samples compared to the dominance of the 4-ring concentration mass in the soot with contributions to that soot mass from the 3-ring and then 5-ring PAH mass (Figure 6a and b). Expressing the n-ring concentration mass as a relative percentage proportion of the total PAH mass furnishes a more normalised comparison of the n-ring fingerprint composition differences between dust and soot samples (Figure 6c and d). The dust dataset exhibits a marked decline from the dominance of the 2-ring mass to declining contributions from successively higher n-ring mass. Whilst recognising the inter-quartile and overall ranges in the individual n-ring percentages are quite large, especially for the 2-ring, the median dust PAH mass proportional composition calculated is: 84% 2-ring: 11% 3-ring : 4% 4-ring : 1% 5-ring PAH (with 6-ring trace). The soot dataset (Figure 6d) exhibits a clear 4-ring peak proportion and a notably small inter-quartile and overall range in observed individual n-ring percentages (Figure 6d). This low variation endorses the median soot PAH mass composition calculated is reasonably representative of all soots sampled, this being: 0.1% 2-ring, 20% 3-ring, 61% 4-ring, 14% 5-ring, 5% 6-ring PAH. This ratio hence appears to offer a well-constrained proportional PAH mass fingerprint of the sampled Malawian kitchen soot.

**PAH diagnostic ratios**

PAH diagnostic ratios, commonly used to identify pollution emission sources (Tobiszewski and Namieśnik, 2012; Yunker et al., 2002), are calculated for the soot and dust datasets (Table 1). Ratio comparison with the provided literature diagnostic ranges corroborates, as anticipated, the soots arise from combustion sources. For three of the four ratios, all samples are categorised in the ‘Solid/grass/wood/coal’ category range. For the other ratio, FLT / FLT+PYR, all samples are indicative of combustion sources, with some ratio just within the above category and the remainder a touch outside (the mean plus standard deviation equates to the lower threshold of that category). Comparison with the example literature combustion ratio given likewise supports wood-related sources (Table 1). Mean ratio for the dust dataset all fall in the combustion ‘Solid/grass/wood/coal’ category. Individual dust ratios could not be calculated for all samples (where relevant PAH were below detection), nevertheless 80% of those calculated were in the above category (all exceptions were for ANT/178). Use of the PAH diagnostic ratios thus usefully confirms the influence of wood-related combustions source for kitchen soots, as expected, but also the dusts. This is consistent with the rural environment and the low expected, still possibly masked, influence of other PAH sources.

Comparison of the two ICS types where multiple soot samples were taken (PCI and Chitetzo stoves) reveals similar ranges in the various PAH ratios and hence their distinctive influence is not apparent (Table 1). In fact, once the outlier low total PAH sample is removed (that yields anomalous ratio), variation in ratio for the entire soot dataset is small with standard deviations corresponding to just 3–7% of the ratio mean. This again points to a reasonable consistent PAH fingerprint regardless of the ICS sampled, and despite the wide variation in total PAH of the soot sampled.

**Improved cookstove type influence on soot PAH**

Using Figure 4a to compare variation inherent to a specific ICS type, there appears considerable variation in kitchen soot total PAH concentrations, especially for the Chiteteto (by a factor of 50 (or 9 ignoring the anomalous low sample 3 concentration)), but also for the PCI (factor of 4). Hence, there must be other influences to cookstove type. These influences were not assessed, but could include variable modes of user operation of a specific ICS type, varying fuel type, and spatial variation in PAH occurrence within a household soot. Isolated sampling of the other ICS types precludes any definitive statements on these factors. It was noted that the Bricette and Aliva stoves show similar total PAH that compare to the highest concentration observed from the PCI stove dataset (Figure 4a). In addition, the single sample from the Esperanza stove is prominent for it being the highest total PAH surveyed.

In terms of varying PAH composition fingerprints, the absolute individual PAH concentrations vary within and between ICS type in accordance with the overall variation in PAH (Figure 4a). The key finding displayed by Figure
6d of little variation of the entire soot dataset from the median soot PAH mass proportional composition, means that differences in proportional n-ring PAH fingerprints between the various ICS types may potentially be minimal (endorsed by the detail of Figure 4b and n-ring proportions in Figure 4c). Generally, the fingerprints are quite comparable without obvious differences between, or within ICS types. Nevertheless, some further observations can be made. For instance, the three highest total PAH Chitetezo samples (-12, -13 and -14) exhibit the maximum 3-ring proportions (Figure 4c) due to the disproportionately high PHE concentrations compared to other samples (Figure 4a). Whist such observations appear minor, they suggest possible scope for diagnostic insight from more detailed evaluation of the 16-PAH fingerprint.

**Principal components analysis (PCA)**

Discrimination of individual PAH influence is further examined through PCA. Figure 7 plots PC scores for the soot samples with an inset showing the PC scores for the dust dataset and their local extent within the former (Figure 7a [soot samples are labeled with a 'b' to distinguish from similar numbered dust samples]). Loading plots for the dust (Figure 7b) and soot (Figure 7c) are also shown for the individual PAH. The maximum total PAH concentration Esperanza stove (Sample 7) was an outlier in the PC scores for the soot samples (Figure 7a); its positioning is attributed to the influence of high PYR (Figure 4a and Figure 7c). Otherwise, most soot samples cluster in the area labeled ‘A’, inferring similar individual PAH concentrations in soot samples within those specified clusters. The remaining soot samples are the aforementioned three highest total PAH Chitetezo samples, 12, 13 and 14 with the former pair at cluster locality ‘B’ and the latter sample 14, somewhat outlying from there (Figure 7a). Their positioning is consistent with the influence of higher PHE noted above and apparent on the loading plot (Figure 7c).

The N-dominated dust samples (Figure 7b) are shown
Table 1. PAH diagnostic ratios observed for kitchen soot and household dust (mean) samples compared to literature diagnostic ranges for petroleum and combustion sources and example environmental samples.

<table>
<thead>
<tr>
<th></th>
<th>'ANT/178'</th>
<th>'BaA/228'</th>
<th>'ANT+PHE'</th>
<th>FLT+PYR</th>
<th>BaA+CHR</th>
<th>IP+BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuels/oil products:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- petroleum</td>
<td>&lt; 0.1</td>
<td>&lt; 0.4</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2 (&lt; 0.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Combustion sources:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Liquid/petroleum fossil fuel</td>
<td>&gt; 0.1</td>
<td>0.4-0.5</td>
<td>&gt; 0.35</td>
<td>0.2-0.5 (0.1-0.3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Solid/grass/wood/coal</td>
<td>&gt; 0.1</td>
<td>&gt; 0.5</td>
<td>&gt; 0.35</td>
<td>&gt; 0.5 (&gt; 0.3)</td>
<td></td>
<td></td>
</tr>
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</table>

**Literature diagnostic ranges**

<table>
<thead>
<tr>
<th>Source</th>
<th>ANT / ANT+PHE</th>
<th>FLT / FLT+PYR</th>
<th>BaA / BaA+CHR</th>
<th>IP / IP+BP</th>
</tr>
</thead>
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<tr>
<td>Fuels/oil products:</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- petroleum</td>
<td>&lt; 0.1</td>
<td>&lt; 0.4</td>
<td>&lt; 0.2</td>
<td>&lt; 0.2 (&lt; 0.1)</td>
</tr>
<tr>
<td>Combustion sources:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- Liquid/petroleum fossil fuel</td>
<td>&gt; 0.1</td>
<td>0.4-0.5</td>
<td>&gt; 0.35</td>
<td>0.2-0.5 (0.1-0.3)</td>
</tr>
<tr>
<td>- Solid/grass/wood/coal</td>
<td>&gt; 0.1</td>
<td>&gt; 0.5</td>
<td>&gt; 0.35</td>
<td>&gt; 0.5 (&gt; 0.3)</td>
</tr>
</tbody>
</table>

**ICS sample (Total PAH)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCI</th>
<th>(μg/g)</th>
<th>ANT / ANT+PHE</th>
<th>FLT / FLT+PYR</th>
<th>BaA / BaA+CHR</th>
<th>IP / IP+BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCI – 1</td>
<td>(52 μg/g)</td>
<td>0.21</td>
<td>0.50</td>
<td>0.52</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>PCI – 2</td>
<td>(73 μg/g)</td>
<td>0.23</td>
<td>0.48</td>
<td>0.55</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>PCI – 10</td>
<td>(100 μg/g)</td>
<td>0.21</td>
<td>0.47</td>
<td>0.47</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>PCI – 9</td>
<td>(156 μg/g)</td>
<td>0.22</td>
<td>0.49</td>
<td>0.52</td>
<td>0.73</td>
<td></td>
</tr>
<tr>
<td>PCI – 11</td>
<td>(226 μg/g)</td>
<td>0.18</td>
<td>0.46</td>
<td>0.51</td>
<td>0.62</td>
<td></td>
</tr>
<tr>
<td>Chitetzo – 3</td>
<td>(14 μg/g)</td>
<td>[outlier]</td>
<td>0.37</td>
<td>0.54</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>Chitetzo – 4</td>
<td>(76 μg/g)</td>
<td>0.21</td>
<td>0.47</td>
<td>0.54</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>Chitetzo – 15</td>
<td>(107 μg/g)</td>
<td>0.19</td>
<td>0.51</td>
<td>0.51</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>Chitetzo – 6</td>
<td>(194 μg/g)</td>
<td>0.21</td>
<td>0.47</td>
<td>0.51</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>Chitetzo – 14</td>
<td>(549 μg/g)</td>
<td>0.21</td>
<td>0.48</td>
<td>0.53</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>Chitetzo – 13</td>
<td>(595 μg/g)</td>
<td>0.18</td>
<td>0.47</td>
<td>0.53</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>Chitetzo – 12</td>
<td>(678 μg/g)</td>
<td>0.21</td>
<td>0.50</td>
<td>0.53</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>Brickette – 8</td>
<td>(209 μg/g)</td>
<td>0.19</td>
<td>0.49</td>
<td>0.53</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>Aleva – 5</td>
<td>(210 μg/g)</td>
<td>0.21</td>
<td>0.47</td>
<td>0.51</td>
<td>0.68</td>
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<tr>
<td>Esperanza – 7</td>
<td>(815 μg/g)</td>
<td>0.20</td>
<td>0.46</td>
<td>0.54</td>
<td>0.62</td>
<td></td>
</tr>
</tbody>
</table>

**Kitchen soot samples**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCI</th>
<th>(μg/g)</th>
<th>ANT / ANT+PHE</th>
<th>FLT / FLT+PYR</th>
<th>BaA / BaA+CHR</th>
<th>IP / IP+BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCI – 1</td>
<td>(52 μg/g)</td>
<td>0.22 ± 0.045</td>
<td>0.48 ± 0.021</td>
<td>0.54 ± 0.064</td>
<td>0.67 ± 0.039</td>
<td></td>
</tr>
<tr>
<td>PCI – 2</td>
<td>(73 μg/g)</td>
<td>0.20 ± 0.015</td>
<td>0.48 ± 0.016</td>
<td>0.52 ± 0.019</td>
<td>0.67 ± 0.039</td>
<td></td>
</tr>
</tbody>
</table>

**Household dust sample set**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCI</th>
<th>(μg/g)</th>
<th>ANT / ANT+PHE</th>
<th>FLT / FLT+PYR</th>
<th>BaA / BaA+CHR</th>
<th>IP / IP+BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Household dust mean</td>
<td></td>
<td>0.13 ± 0.041</td>
<td>0.55 ± 0.092</td>
<td>below detection</td>
<td>0.51 ± 0.021</td>
<td></td>
</tr>
<tr>
<td>(n = 23)</td>
<td></td>
<td>(n = 35)</td>
<td>(n = 0)</td>
<td>(n = 7)</td>
<td></td>
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**Literature combustion data (for comparison)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PCI</th>
<th>(μg/g)</th>
<th>ANT / ANT+PHE</th>
<th>FLT / FLT+PYR</th>
<th>BaA / BaA+CHR</th>
<th>IP / IP+BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood soot (n=2)</td>
<td></td>
<td>0.26</td>
<td>0.5</td>
<td>0.46</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>Wood (n=19)</td>
<td></td>
<td>0.19</td>
<td>0.51</td>
<td>0.46</td>
<td>0.64</td>
<td></td>
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<tr>
<td>Grasses (n=6)</td>
<td></td>
<td>0.17</td>
<td>0.58</td>
<td>0.46</td>
<td>0.58</td>
<td></td>
</tr>
<tr>
<td>Kerosene (n=3)</td>
<td></td>
<td>0.14</td>
<td>0.5</td>
<td>0.37</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Bush fire (n = not indicated)</td>
<td></td>
<td>0.61</td>
<td>0.23</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


by the Figure 7a inset locality to plot as a very tight cluster at locality 'C', close to 'A' within the soot plot. This demonstrates that there is minimal variation in the concentration of PAHs in dust compared to soot samples. The dust samples plot closest to the soot sample 3 Chitetze stove concentration (plotted 3b on the Figure 7a dust inset for reference); this is the anomalously low minimum total PAH soot sample (Figure 4a). The other soot samples that plot closest to the dust cluster (soot samples 1, 2, 4, 9 and 10) form the lower total PAH samples of the PCI and Chitetze stove sample sets.

**Other compounds present**

Whilst not the study focus, methoxyphenols and organo-
sulfur compounds were identified in some dust and soot samples in the course of the GC-MS analysis. Each are associated with significant human health effects when present in the ambient air environment. Brief observations follow.

Methoxyphenol compounds are emitted from wood burning (pyrolysis of lignin) and have long been used as biomarkers of smoke exposure from wood burning with human exposure typically via inhalation (Clark et al., 2007). Methoxyphenols were detected in seven soot samples, but no dust samples. Sample peaks areas relative to the internal standard are shown in Figure 8a.

Figure 7. Soot samples principal component analysis (modified from Chidziwisano, 2012): (a) score plot for soot samples with inset showing dust samples; (b) loading plot for dust samples; (c) loading plot for soot samples.
that illustrates increased methoxyphenol concentrations occur with elevated concentrations of total PAH.

Atmospheric emission of sulfur compounds from biomass burning depends on the sulfur content and quantity of volatile sulfur in the biomass with plant type and combustion temperature critically controlling volatile sulfur emitted (Badr and Probert, 1994). Organo-sulfur related compounds were identified in 10 samples, of which 9 were dust samples at generally very minimal (non-quantified) concentrations with low levels of total PAH (Figure 8b). The only soot sample (9 from a PCI stove) that contained organo-sulphur had a low soot (third lowest) total PAH. The general conclusion is that low organo-sulphur concentrations were found in around a quarter of the low PAH dust samples with no evidence of occurrence in moderate to higher PAH concentration kitchen soot.

**Conclusions**

In line with the Government of Malawi policy and SDG agenda, the present decade is witnessing a marked increase in ICS use across Malawi, supported by a growing body of Malawian research. Similar increase is apparent across the developing world. This exploratory study has novelty within the enabling Malawian research effort, and internationally, examining risks posed by PAHs on inhalable PM posed to households that may remain in spite of ICS adoption. Cooking areas in most
rural Malawian households are usually integral to the main house, often poorly ventilated, and pose greater HAP exposure risks to women and children more commonly present. Although increasing use of ICS facilities over traditional fires is reasonably expected to reduce exposure risks. Recent studies cited increasingly confirm that exposure risks to harmful PM remain significant and variable across ICS type and household-use environments. There is, however, a lack of datasets on PM-bound PAH contents and fingerprint compositions associated with ICS use; these appear increasingly needed given PM emission variability and less-than-expected health benefits of ICS interventions to gain understanding of specific chemical-based risks. This exploratory study through a straightforward approach of reconnaissance sampling of household dusts and kitchen soot has demonstrated that PAH associated with inhalable PM may continue to pose health risks to household occupants, even when ICS use is adopted.

This study confirms that total PAH for household dusts was always low, with means around 2 μg/g and volatile 2-ring naphthalene always dominant. Kitchen soot samples exhibited total PAH means some two orders of magnitude higher, around 200 μg/g to a maximum of 815 μg/g. Total PAH in kitchen soot displayed a wide range, both across the entire soot dataset, and for individual ICS type. Trends were not obvious with ICS type (recognising limited sample size in this exploratory study). Despite the wide range in soot total PAH and various ICS sampled, the soot PAH fingerprint appeared well constrained with most soot having n-ring fingerprints close to the median soot of: 0.1% 2-ring, 20% 3-ring, 61% 4-ring, 14% 5-ring, 5% 6-ring PAH. In addition, commonly used diagnostic PAH ratios were quite similar across the soot dataset. These ratio for soot and dusts, confirmed the expected influence of wood-related combustion sources for the PAH and is consistent with the rural African environment confirming the anticipated current low influence of other PAH sources. Increased total PAH and greater proportions of the higher carcinogenicity, 4- to 6-ring PAH than less toxic 2- to 3-PAH within soot causes their inhalation and ingestion to pose much greater health risks than the coarser, but still inhalable, PM dusts. Exposure risks remain greatest for women and children who spend more time in the indoor environment.

With the very limited developing-world availability of analytical facilities for micro-organic pollutant (incl. PAH) analysis in Malawi (and likely elsewhere) and greater ease of PM measurement, it is expected PM measurements will remain the primary metric for management of PM-associated pollutants such as PAH. This exploratory study, however, endorses the need for household-based research studies that characterise not only factors that control PM emissions, but also within those assessments, characterisation of the total PAH, its fingerprint composition and temporal/spatial PAH variation within PM emissions driving the chemical-based health risks. Whilst the soot PAH fingerprint (n-ring proportions and diagnostic PAH ratios) observed appear quite consistent and may usefully underpin PAH-related health risk assessments, this consistency requires evaluation across larger datasets. Of key importance, is to understand the factors that control total PM emission quantities and associated total PAH that may cause significant variation between, and within, ICS types and modes and conditions of use; and in turn, marked variation in HAP and differing PAH exposure risks to individual households.

Hence relationships between PAH risks and more facile PM measurements need to be investigated within the context of expanding ICS use and possible influence of the plethora of ICS designs, operational modes, building/ventilation design, variable fuel sources and recognised non-optimal use. There is need for household studies to sample the airborne PM and associated PAH concentrations and fluxes. A variety of study types are possible to include before and after ICS installation to households (with controls). Long-term studies to ensure reductions in emissions and health risks are sustained as well as cross-sectional studies where PAH-related aspects of ICS design/efficiency HAP or health outcomes are measured simultaneously in households with traditional stoves and households with ICSs in a similar geographic area (Chaigneau, 2012). It will be important to address here the concern noted by Thomas et al. (2015) that many households continue to use both traditional fires/stoves and ICS, even reverting back to the former. Such studies are vital to the optimisation of ICS designs and household user practice improvements to secure delivery of SDG 3 and SDG 7.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ACKNOWLEDGEMENTS

The authors appreciate Prof. Anthony Grimason and Vincent Doyle of Concern Universal for arranging the collection and transportation of all soot samples analysed in this study. They also gratefully acknowledge the support in final manuscript preparation provided by the Scottish Government under the Scottish Government Climate Justice Fund Water Futures Programme research grant HN-CJF-03 awarded to the University of Strathclyde (R.M. Kalin).

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Understanding nexuses between precipitation changes and climate change and variability in semi-arid lowlands of Mwanga District, Tanzania

Bagambilana Francis Rweyemamu and Rugumamu William Mulokozi*

Department of Geography, College of Humanities, University of Dar es Salaam, Tanzania.

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Contextually, precipitation fluctuated due to climate variability and evolved due to emissions of anthropogenic greenhouse gases and land-use changes since the industrial revolution in the 1880s. However, some studies problematize that there is little understanding of nexuses between precipitation changes and climate change and variability in tropical Africa. Therefore, this paper sought to assess such linkages in semi-arid lowlands of Mwanga District, Tanzania. The findings revealed statistically significant decrease of annual rainfall, Kendall’s tau $r_\tau (44) = -0.230, p = .019$ and Kendall’s tau $r_\tau (39) = -0.223, p = .024$, at Same Meteorological station (1970 to 2009 and 2012 and 2015) and Nyumba ya Mungu Meteorological stations (1977 to 2015), respectively; thus confirming occurrence of human-induced climate change in the study area. Also, the findings revealed statistically significant correlations between amounts of rainfall (September – February) and Niño 3.4 index and between amounts of rainfall (October – December) and dipole mode index at both stations, hence confirming that precipitation changes during short rainy seasons ($Vuli$) in the lowlands were significantly influenced by cycles of El Niño-southern oscillation and Indian Ocean dipole. Besides, branched and isoprenoid tetraether (BIT) indices revealed that wettest conditions, due to climate variability. This occurred from 650 to 950 CE (common era), 1550 to 1700 CE, 22 to 25 ka BP (before present, present defined as 1950). Whereas, driest conditions occurred from 1968 to 1974, 1780 to 1820 CE, 1170 to 1300 CE (between ca. 0.8 and 0.6 ka BP), 11.7 to 13.1 (the Younger Dryas), 15 to 18 (Heinrich 1 stadial) and 23.4 (Heinrich 2 stadial) ka BP. Lastly, the paper recommends enhancement of traditional and modern-day environmental knowledge systems with regard to weather forecasting and prediction.

Key words: Branched and isoprenoid tetraether index, climate change, climate variability, El Niño-southern oscillation, Indian Ocean dipole, and short rainy season.

INTRODUCTION

According to the intergovernmental panel on climate change (IPCC) (2013), climate fluctuates (climate variability) and evolves (climate change) across space and over time. On the one hand, the main drivers of...
climate variability include the Indian Ocean dipole (IOD), El Niño-southern oscillation (ENSO), Pacific decadal oscillation (PDO) and Atlantic multidecadal oscillation (AMO). Initially driven by land-sea temperature gradients, atmospheric teleconnections of coupled atmosphere-ocean modes of climate variability lead to extreme weather and climate events, such as droughts and floods at local, meso, synoptic, and planetary spatial scales (Pokhrel et al., 2012; IPCC, 2013; Cassou et al., 2018; Yeh et al., 2018). Cassou et al. (2018) explained, for instance, that devastating droughts and famines of the 1970s and 1980s in the Sahel were associated with changing modes of AMO and PDO.

On the other hand, the main drivers of human-induced climate change, as explained by the theory of greenhouse effect, are accumulation of anthropogenic greenhouse gases in the atmosphere and land-use changes (UN, 1992). To the contrary, however, some scientists, including those affiliated with the Heartland Institute (Bast, 2010) and a nongovernmental international panel on climate change (NIPCC) are skeptical of human-induced climate change or deny the existence of a consensus on the science of human-induced climate change (Stewart, 2008; Inhofe, 2012; Brown, 2013; Idso et al., 2016).

It should be understood that this study adopted a definition of climate change as developed by the United Nations framework convention on climate change (UNFCCC). Specifically, UNFCCC stressed that climate change:

‘Means a change of climate which is attributed directly or indirectly to human activity that alters the composition of the global atmosphere and which is in addition to natural climate variability observed over comparable time periods’ (UN, 1992:7).

Indeed, IPCC’s definition reveals that climate change is either caused by natural internal processes/dynamics or external forces, such as modulations of solar cycles (sunspots), volcanic eruptions, orbital parameters (eccentricity, precession, and obliquity), and anthropogenic changes in the composition of the atmosphere and land-use change (IPCC, 2013).

Besides, modeling studies projected that shifts of mean climate would increase the frequency, intensity, duration, spatial extent and timing of some extreme weather and climate events (IPCC, 2012; Ostberg et al., 2018). Higher temperatures would lead to, for instance, increasing rates of evapotranspiration, hence increasing severity of droughts on agricultural systems particularly in semi-arid areas (FAO et al., 2018).

According to IPCC (2013), it is very likely that the global water cycle was affected by anthropogenic influences since the 1960s. Such influences (including increasing atmospheric temperatures) led to increases in atmospheric moisture content, global-scale changes in precipitation patterns over land, and intensification of heavy precipitation over land regions where data were sufficient (medium confidence). Under a representative concentration pathway (RCP)8.5 scenario, mean precipitation will likely decrease in many mid-latitude and subtropical dry regions by the end of the 21st century but will likely increase in many mid-latitude wet regions and in the East African region.

On the contrary, some studies, including those undertaken by human-induced climate change skeptics and deniers, suggested that the frequency and intensity of extreme weather events (droughts, floods, and storms) had either decreased or did not reveal any particular trend during recent decades (Stewart, 2008; Inhofe, 2012; Brown, 2013). A study conducted by Laliberté et al. (2015) explained, that warmer periods including the Medieval Climate Anomaly circa (ca.) 900 - 1200 CE and the 20th/21st centuries were associated with a decrease of extreme weather events and that cool periods including the Little Ice Age ca. 1300 to 1900 CE were associated with an increase of unstable and intense weather. IPCC (2013) and Zheng et al. (2018) also supported such findings.

Besides, Verschuren et al. (2000) explained that there is a need to understand long-term precipitation-climate change and variability nexus in order to enhance, among other things, water-resource and land-use management in semi-arid regions of tropical Africa. Indeed, livelihoods of the majority of people in semi-arid tropical Africa were pegged on rain-fed agricultural systems (encompassing sub-systems of crop, livestock, fishery, and forestry production) that were likely to be exacerbated by the interplay between climate change and variability and non-climate drivers and stressors. It should be noted, however, that an understanding of precipitation-climate change and variability nexus in the region was limited by lack of long-term instrumental time series of precipitation. Also, limited high-resolution and well-dated proxy records, such as ice cores and tree rings particularly in areas experiencing bimodal rainfall regime due to biannual passage of inter-tropical convergence zone (ITCZ) (Verschuren et al. 2009).

Indeed, majority of residents in semi-arid lowlands of Mwanga District, Tanzania, which covered 69.4% of the total area of 264,100 ha frequently, faced climate-related stressors, such as meteorological/agricultural droughts, dry spells, and floods (MDC, 2016). These has led to water shortages, land degradation, frequent crop failures, famines (locally known as Nzota), and death of domestic animals (Mvungi, 2008; Mashingo, 2010; IFRC and RCS, 2013). Such attributes suggested that precipitation changes in semi-arid lowlands of Mwanga District either reflected human-induced climate change or natural climate variability or both climate change and variability. Coupled with instrumental time series of rainfall and high resolution and well-dated branched and isoprenoid tetraether (BIT) indices for paleo-precipitation, this study...
was undertaken in order to understand linkages between precipitation changes in semi-arid lowlands of the district and both climate change and modes of climate variability (El Niño-southern oscillation and Indian Ocean dipole) across different temporal scales.

**METHODOLOGY**

**Study area**

Mwanga district (Figure 1) is one of the seven districts of Kilimanjaro Region in northeastern Tanzania and it extends...
between latitudes 3°46’S and 3°47’ S and between longitudes 37°35’E and 37°50’E (MDC, 2016). Furthermore, the district covers 2,641 km² and borders Moshi Rural district and the republic of Kenya in the north, republic of Kenya and Lake Jipe in the East, Same district in the South, and Simanjiro district, NyM Reservoir, and Moshi rural district in the West. Specifically, the district’s land areas cover 2,558.6 km² while water bodies cover 82.4 km². With regard to water bodies, the NyM reservoir covers 56 km² and Lake Jipe covers 26.4 km² (MDC, 2016).

Furthermore, the regime of rainfall in Mwanga district was bimodal and largely controlled by annual shift in the position of ITCZ and the low-level northeasterly and southeasterly trade winds/monsoons (Moernau et al., 2010). Specifically, strong and dry winds tended to blow from East to the West (MDC, 2016). Additionally, both ITCZ and trade winds/monsoons were driven by latitudinal differences for radiation, which was received at the Earth’s surface (Moernau et al., 2010). Consequently, long rains (Mbua ja Mashikaa in Pare language) were experienced from March to June and short rains (Mbua ja Vhuri in Pare language) were experienced from October to January (MDC, 2016).

In addition, the amount of rain varied spatially. Highest amount of rain (800-1350 mm/year) fell in the North Pare Mountains and on its eastern windward slopes to the Indian Ocean and lowest amount of rain (400-600 mm/year) fell in the eastern and western lowlands (URT, 2004; MDC, 2016). Besides, temperatures ranged from an average minimum of 14°C between July and August to a maximum average of 32°C between January and February. According to IPCC (2013), shifts of climate mean(s) can reliably be detected by analyzing time series data that cover a period of about 50 years. In this regard, attempts were made to source rainfall time series covering longer time periods from meteorological/weather stations within Mwanga District or nearest meteorological/weather stations in Same District (Figure 1). It is worth pointing out that, Pare District was split in 1978 to form Mwanga District in the northern part (MDC, 2016) and Same District in the southern part.

However, rainfall time series for NyM Meteorological Station (station code 9337090) and Same Meteorological Station (station code 9437003) that were sourced from Tanzania meteorological agency (TMA) and Pangani basin water board (PBWB) covered 39 and 44 years, respectively. Indeed, both stations are found in semi-arid lowlands but attempts to harmonize attendant time series would have decreased reliability of analyses for detecting climate change. Otherwise, the same time series were useful for establishing inter-annual climate variability. Besides, rainfall time series covering a period of 62 years (1938 to 1999) at Moshi Meteorological Station (station code 9337004) were sourced from Rehr (2003) as originally sourced from PBWB. Indeed, such time series were used occasionally for comparison with time series for NyM and Same Meteorological Stations. Generally, the computed standardized coefficients of skewness and kurtosis for rainfall time series were positively skewed and < 1.96, hence the coefficients revealed approximate normal distribution.

Also, time series of Niño 3.4 index (sea surface temperature anomalies averaged for areas extending between 5°N and 5°S and between 120° and 170°W in the tropical Pacific Ocean), covering a period of 46 years (1970 to 2015) were accessed through online visits from the national oceanic and atmospheric administration (NOAA). Similarly, time series of dipole mode index (DMI) covering a period of 46 years (1970 to 2015) were accessed through online visits from NOAA. Indeed, DMI time series represented anomalous SST gradient between the western equatorial Indian Ocean (extending between 50°E and 70°E and between 10°S and 10°N) and the southeastern equatorial Indian Ocean (extending between 90°E and 110°E and between 10°S and 0°N).

Moreover, time series for well-resolved BIT index covering periods of the last 2.2 and 25 ka for a hydroclimate of Lake Challa (Figure 1) were accessed online as originally used by Buckleys et al. (2016) and Sinninghe Damsté et al. (2012), respectively. It should be noted that Lake Challa is at an altitude of 880 m a.s.l on the lower east slope of Mount Kilimanjaro and along the border between Tanzania and Kenya. Trend analysis (moving averages) was conducted on BIT time series in order to establish patterns of paleo-precipitation with regard to past cycles of climate variability. Moreover, datasets of rainfall, Niño 3.4 index, DMI, and BIT were entered into spreadsheets (IBM SPSS 20 and or 2007 Excel software) and processed into desired formats. Specifically, datasets of rainfall were cleaned for errors and missing observation values before conducting data analysis. In this regard, the main data cleaning methods were spot-checking, reviewing, and logic checks. It should be noted, however, that a period of two years (January 2010 to December 2011) with missing rainfall time series at Same Meteorological Station, as original time series had not been corrected, was not included in the analysis of meteorological data. Additionally, spatial interpolation could not be conducted with rainfall time series from three meteorological stations (Same, NyM, and Moshi Airport) (Figure 1) as there were no other meteorological/weather stations with relatively longer time series in Mwanga District. According to Tao et al. (2009), the use of deterministic methods (including Inverse Distance Weighted and Spline) and geostatistical methods (including Krigeing) of spatial interpolation of climate parameters is worthwhile when there is sufficient density of meteorological/weather stations.

Besides, cleaned datasets of quantitative data were analyzed in IBM SPSS 20 and or 2007 Excel's Analysis ToolPak by computing univariate and bivariate statistics. Specifically, univariate statistics were computed using the following formulas:

1) Mean ($\bar{M}$)

$$\bar{X} = \frac{1}{n} \sum_{i=1}^{n} x_i$$  
(1)

Where, $\bar{X}$ = sample mean, $n$ = number of values, $x_i$ = individual value of the sample or measurement (where $i$ goes from 1 to $n$).

2) Range

$$n = x_n - x_1$$  
(2)

Where, $n$ = range, $x_n$ = maximum value, $x_1$ = minimum value.

3) Standard deviation (SD)

$$s = \sqrt{\frac{\sum(x_i - \bar{X})^2}{n-1}}$$  
(3)

Where, $s$ = standard deviation, $\bar{X}$ = sample mean, $n$ = number of values, $x_i$ = individual value of the sample or measurement (where $i$ goes from 1 to $n$).

4) Anomaly (deviation score)

$$d = x - \bar{X}$$  
(4)

where, $d_i$ = deviation score for the $i$th observation in a set of observations, $x$ = raw score for observation in a set of observations, $\bar{X}$ = mean of all values in a set of observations.
5) Coefficient of variation

\[ CV = \frac{S}{\bar{x}} \]  

(5)

Where, \( CV \) = coefficient of variation, \( S \) = standard deviation, \( \bar{x} \) = sample mean.

Furthermore, findings on trends/moving averages were also presented as linear graphs. Additionally, statistical significance of Kendall’s tau test was undertaken basing on the following hypotheses:

\( H_0 \): There was no trend (data is independent and randomly ordered).

\( H_1 \): There was a trend.

In this regard, Kendall’s tau \( r \) was computed using the following formula:

6) Kendall’s tau \( r \),

\[ r = \frac{n_z - n_d}{\frac{1}{2}n(n-1)} \]  

(6)

Where, \( T = \) Kendall’s tau, \( n = \) sample size, \( n_z = \) number of concordant pairs, \( n_d = \) number of discordant pairs.

Besides, bivariate analyses encompassed computation of Pearson’s correlation coefficient through the following formula:

7) Pearson’s correlation coefficient:

\[ r = \frac{n \sum xy - \sum x \sum y}{\sqrt{\left(n \sum x^2 - (\sum x)^2\right)\left(n \sum y^2 - (\sum y)^2\right)}} \]  

(7)

Where, \( n = \) number of pairs of score, \( \sum xy = \) sum of the products of paired scores, \( \sum x = \) sum of \( x \) scores, \( \sum y = \) sum of \( y \) scores, \( \sum x^2 = \) sum of squared \( x \) scores, \( \sum y^2 = \) sum of squared \( y \) scores.

It is worth pointing out that alpha level (\( \alpha \)) was set at 0.05 and the central limit theorem was invoked since the sample size was sufficiently large (usually \( N \geq 30 \)) (Field, 2013). Consequently, the findings based on analysis of quantitative data were largely presented in tables and graphs.

Besides, time series of BIT (branched and isoprenoid tetraether) indices, based on GDGTs (glycerol dialkyl glycerol tetraethers) as proxies for paleo precipitation of Lake Challa area (Figure 1), were sourced through online visits. Indeed, the time series covering a period of the last 2.2 ka were originally used by Buckles et al. (2016) and time series covering a period of the last 25 ka were originally used by Sinninghe Damsté et al. (2012). Additionally, authors through the following formula computed the time series:

8) BIT Index

\[ BIT_{index} = \frac{[VI] + [VII] + [VIII]}{[V] + [VI] + [VII] + [VIII]} \]  

(8)

Where, \( VI = brGDGT\ VI, \ VII = brGDGT\ VII, \ VIII = brGDGT\ VIII, \ V = \) Crenarchaeol isoGDGTs.

\( br = \) branched, \( iso = \) isoprenoid, and \( GDGT = \) glycerol dialkyl glycerol tetraether

In this regard, times with high BIT values implied existence of drier conditions and times with low BIT values implied existence of wetter conditions (Damsté et al., 2012; Buckles et al., 2016).

**RESULTS AND DISCUSSION**

This section presents findings and discussions of findings. Specifically, it focuses on instrumental rainfall changes in the study area, nexuses between instrumental rainfall changes in the study area and ENSO–southern oscillation and Indian Ocean dipole coupled with BIT indices for paleo-precipitation changes in the study area.

**Instrumental rainfall changes in the study area**

To begin with, mean annual rainfall at Same Meteorological Station decreased by 235.2 mm from 631.1 mm with a relatively higher SD of 239.4 (1970 to 1979) to 395 mm with a relatively lower SD of 73.2 (2012 to 2015) (Table 1). Similarly, mean annual rainfall at NyM Meteorological Station decreased by 250.3 mm from 611.6 mm with a relatively higher SD of 170.7 (1977–1997) to 361.3 mm with a relatively lower SD of 77.1 (2010 to 2015) (Table 2). Generally, the variability of annual rainfall at NyM Meteorological Station, typified by SD of 157.5 for a mean of 342.9 mm and an average coefficient of variation of 0.5 (2017 to 2015), was relatively higher than the variability of rainfall at Same Meteorological Station. This was typified by SD of 202.1 for a mean of 540.5 mm and an average coefficient of variation of 0.4 (1970 to 2009 and 2012 to 2015) (Tables 1 and 2).

Also, the findings revealed, during a period of 44 years (1970 to 2009 and 2012 to 2015), increasing negative anomalies of annual rainfall from a reference value of 567.2 mm (an average for a period of 30 years from January 1977 to December 2006) at Same Meteorological Station (Figure 2). Additionally, the fitted linear trend line is statistically significant at alpha level, \( \alpha \), of 0.05 (Kendall’s tau \( r \) = 0.230, \( p = 0.019 \)). Similarly, the findings revealed, during a period of 39 years (1977-2015), increasing negative anomalies of annual rainfall from a reference value of 345.5 mm (an average for a period of 30 years from January 1977 to December 2006) at NyM Meteorological Station (Figure 3). In addition, the fitted linear trend line is statistically significant at alpha level, \( \alpha \), of 0.05 (Kendall’s tau \( r \) = 0.223, \( p = 0.024 \)).

In this regard, positive and negative anomalies of annual rainfall typified annual and inter-annual climate variability. Additionally, increasing negative anomalies of annual rainfall decreased mean annual rainfall, which led
Table 1. Decadal changes in mean annual rainfall at Same Meteorological station, 1970 to 2009 and 2012 to 2015.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>M</td>
<td>540.5</td>
<td>631.1</td>
<td>559.3</td>
<td>528.5</td>
<td>500.7</td>
<td>395.9</td>
</tr>
<tr>
<td>SD</td>
<td>202.1</td>
<td>239.4</td>
<td>122.9</td>
<td>228.4</td>
<td>219.0</td>
<td>73.2</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>0.4</td>
<td>0.4</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Range</td>
<td>808.7</td>
<td>754.4</td>
<td>391.6</td>
<td>675.5</td>
<td>753.9</td>
<td>169.4</td>
</tr>
<tr>
<td>Minimum</td>
<td>265.3</td>
<td>319.6</td>
<td>376.5</td>
<td>299.7</td>
<td>265.3</td>
<td>293.3</td>
</tr>
<tr>
<td>Maximum</td>
<td>1074.0</td>
<td>1074.0</td>
<td>768.1</td>
<td>975.2</td>
<td>1019.2</td>
<td>462.7</td>
</tr>
</tbody>
</table>

Source of data: TMA and PBWB.

Table 2. Decadal changes in mean annual rainfall at NyM Meteorological station, 1977 – 2015.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>342.9</td>
<td>611.6</td>
<td>377.6</td>
<td>332.6</td>
<td>226.6</td>
<td>361.3</td>
</tr>
<tr>
<td>SD</td>
<td>157.5</td>
<td>170.7</td>
<td>112.5</td>
<td>145.9</td>
<td>142.1</td>
<td>77.1</td>
</tr>
<tr>
<td>Coefficient of variation</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Range</td>
<td>731.1</td>
<td>338.2</td>
<td>400.8</td>
<td>547.8</td>
<td>487.5</td>
<td>215.4</td>
</tr>
<tr>
<td>Minimum</td>
<td>63.2</td>
<td>456.1</td>
<td>198.1</td>
<td>84.3</td>
<td>63.2</td>
<td>272.5</td>
</tr>
<tr>
<td>Maximum</td>
<td>794.3</td>
<td>794.3</td>
<td>598.9</td>
<td>632.1</td>
<td>550.7</td>
<td>487.9</td>
</tr>
</tbody>
</table>

Source of data: TMA and PBWB.

Figure 2. Annual rainfall anomalies for Same Meteorological Station, 1970– 2009 and 2012 – 2015.
Source of data: TMA and PBWB.


<table>
<thead>
<tr>
<th>Ordinal by Ordinal</th>
<th>Value</th>
<th>Asymp. Std. Error</th>
<th>Approx. T</th>
<th>Approx. Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kendall’s tau-b</td>
<td>-0.230</td>
<td>0.098</td>
<td>-2.349</td>
<td>0.019</td>
</tr>
<tr>
<td>Kendall’s tau-c</td>
<td>-0.230</td>
<td>0.098</td>
<td>-2.349</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Source of data: TMA and PBWB.

Source of data: TMA and PBWB.
to climate change. Indeed, rainfall decreased faster at NyM Meteorological Station (slope $-4.900$ mm y$^{-1}$ and change is explained by 12.5% of the observed variance) than at Same Meteorological Station (slope $-4.186$ mm y$^{-1}$ and change is explained by 7% of the observed variance) (Figures 2 and 3).

For comparison purposes, the findings did not reveal, during a period of 62 years (1938 – 1999), increasing negative anomalies of annual rainfall from a reference value of 905 mm (an average for a period of 30 years from 1967 to 1996) at Moshi Airport Meteorological Station (Figure 4). Additionally, the fitted linear trend line is non-statistically significant at alpha level, $\alpha$, of 0.05 (Kendall’s tau $\tau$ (62) = .021, $p = .810$) (Table 5).

It is worth pointing out that climate change is partly caused by land-use/land cover changes (UN, 1992). Furthermore, statistically significant decrease of annual rainfall at both Same and NyM Meteorological stations could partly be explained by land-use/land cover changes. In this regard, a study conducted by Misana et al. (2012) in Kilimanjaro Region (also encompassing semi-arid areas in Mwanga District) revealed, through analyses of satellite images dated 1973, 1984 and 1999/2000, expansion of cultivated areas in the southern and eastern lowlands of Mount Kilimanjaro. This was at the expense of natural vegetation, particularly natural forests in the highlands of Mount Kilimanjaro. Specifically, cultivated areas increased from 54% in 1973, to 62 and 63% in 1984 and 2000, respectively. The main underlying drivers for such land-use/land cover changes were demographic, government policies, socio-economic/cultural factors encompassing land-tenure system, institutional factors, technological change and infrastructure development.

Besides, a study conducted by Huang et al. (2016) revealed that precipitation had decreased by 57 mm in the newly formed semi-arid regions of East Asia during a 61-year period from 1948 to 2008. Additionally, potential evapotranspiration had increased by 132 mm in the same regions and same timescale. A decrease of precipitation and concomitant increase of potential evapotranspiration led to a considerable decrease of aridity index, computed as the ratio of precipitation to potential evaporation, implying an increase of drying trends in the newly formed semi-arid regions of East Asia. The consistency of precipitation patterns with aridity patterns implied precipitation was a key factor influencing aridity index. It is worth pointing out that precipitation had decreased at lesser rate and potential evapotranspiration had increased at lesser rate in the old semi-arid regions of East Asia.

Likewise, a study conducted by Mabhuye et al. (2015)
revealed negative sloping trends for rainfall in most of arid and semi-arid lands of Tanzania during a period from 1975 to 2004. The same study revealed, however, non-significant positive linear trends for annual, MAM (March, April, May), and OND (October, November, December) rainfall for Dodoma during a period from 1960 to 2007.

Besides, a study conducted by IPCC (2013) revealed a high degree of both temporal and spatial variability of precipitation in eastern Africa. Specifically, MAM rainfall had decreased in the region during the previous three decades probably due to rapid warming of the Indian Ocean that led to convection and precipitation over the tropical Indian Ocean and subsidence of drier air over eastern Africa. Additionally, an increasing frequency of dry spells tended to be accompanied with an increasing trend in daily rainfall intensity. Consequently, higher rainfall intensity tended to increase both soil erosion and sediment loads in waterways.

It should be noted, however, that projection of precipitation was much more uncertain than projection of temperature (UNEP, 2012). According to IPCC (2013), an assessment of 12 Coupled Model Intercomparison Project Phase 3 GCMs (general circulation models) over eastern Africa suggested, for instance, a wetter climate with more intense MAM and OND rainy seasons and less severe droughts by the end of the 21st century. During the same time, however, regional climate models indicated that most parts of Kenya, South Sudan, and Uganda would experience drier conditions in August and September due to the weakening of Somali jet and Indian Ocean monsoon. Additionally, it was projected that boreal spring rains would be truncated over eastern Ethiopia, Somalia, Tanzania, and southern Kenya while boreal fall seasons would be lengthened in southern Kenya and Tanzania in the mid-21st century.

**Nexuses between rainfall changes in the study area and El niño–southern oscillation and Indian Ocean dipole**

An evaluation of the linear relationships between ENSO’s Niño 3.4 (five month running mean of extended reconstructed sea surface temperature version 5 (ERSST.v5) anomalies in the Niño 3.4 region from September – February) (Figure 5) and amounts of rainfall

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**Figure 4.** Annual rainfall anomalies for Moshi Airport Meteorological Station, 1938 – 1999. Source of data: Røhr (2003).

**Table 5.** Mann-Kendall’s test for trend of rainfall at Moshi Airport Met Station, 1938 to 1999.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Asymp. Std. Error</th>
<th>Approx. T&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Approx. Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinal by Ordinal</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kendall’s tau-b</td>
<td>0.021</td>
<td>0.086</td>
<td>0.241</td>
<td>0.810</td>
</tr>
<tr>
<td>Kendall’s tau-c</td>
<td>0.021</td>
<td>0.086</td>
<td>0.241</td>
<td>0.810</td>
</tr>
<tr>
<td>N of Valid Cases</td>
<td>62</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* a. Not assuming the null hypothesis.
* b. Using the asymptotic standard error assuming the null hypothesis.

Source of data: Røhr (2003).
for corresponding periods at Same and NyM Meteorological stations was made through hypothesis testing for statistical significance of Pearson’s correlation coefficients.

$H_0$: $\rho = 0$ (there was no linear relationship between ENSO’s Niño 3.4 and amounts of rainfall during periods from September to February).

$H_a$: $\rho \neq 0$ (there was a linear relationship between ENSO’s Niño 3.4 and amounts of rainfall during periods from September to February).

Pearson’s correlation coefficient indicated that there was a significant positive linear relationship between ENSO’s Niño 3.4 and amounts of rainfall (September – February) at Same Meteorological Station, $r(41) = .54$, $p < .001$ (Table 6), which led to rejection of the null hypothesis. Similarly, there was a significant positive linear relationship between ENSO’s Niño 3.4 and amounts of rainfall (September – February) at NyM Meteorological Station, $r(37) = .45$, $p = .004$, which led to rejection of the null hypothesis. Besides, the amounts of rainfall at both stations were highly correlated during a period from September to February, $r(34) = .85$, $p < .001$.

It is worth pointing out that high amounts of rain, 401 mm, 540 mm, and 920 mm, were recorded at Same Meteorological Station from September to February during strong El Niño events of 1972/73, 1982/83, and 1997/98. This was when corresponding Niño 3.4 values were 1.0, 1.3, and 1.4 respectively while low amount of rain, 108.5 mm, was recorded (during the same months) at the same station during a strong La Niña event of 1974/75 when the corresponding Niño 3.4 value was -1.1. Also, high amounts of rain, 421 mm and 598, were recorded (during similar months) at NyM Meteorological Station during strong El Niño events of 1982/83 and 1997/98, when corresponding Niño 3.4 values were 1.3 and 1.4 respectively. However low amounts of rain, 44 and 64 mm, were recorded (during the same months) at the same station during strong La Niña events of 1999/00 and 2000/01 when corresponding Niño 3.4 values were -1.3 and -1.1, respectively.

Similarly, an evaluation of the linear relationships between IOD’s DMI (overall anomalies of DMI averaged for periods from October to December) (Figure 6) and the amounts of OND rainfall at Same and NyM Meteorological stations was made through hypothesis testing for statistical significance of a Pearson’s correlation coefficient.

$H_0$: $\rho = 0$ (there was no linear relationship between IOD’s

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**Figure 5.** ENSO’s Niño 3.4, 1970/71 to 2015/2016. Source of data: NOAA.

**Table 6.** Correlation matrix for ENSO’s Niño 3.4 and rainfall at Same and NyM meteorological Stations.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ENSO’s Niño 3.4 (Sep - Feb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Sep – Feb rainfall at Same Station</td>
<td>0.54**</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Sep – Feb rainfall at NyM station</td>
<td>0.45**</td>
<td>0.85**</td>
</tr>
</tbody>
</table>

**Correlation is significant at the 0.01 level (2-tailed).**
DMI and amounts of OND rainfall.

\[ H_0: \rho \neq 0 \] (there was a linear relationship between IOD's DMI and amounts of OND rainfall).

An analysis using Pearson's correlation coefficient indicated that there was a significant positive linear relationship between IOD's DMI and amounts of OND rainfall at Same Meteorological Station, \( r(42) = .57, p < .001 \) (Table 7), which led to rejection of the null hypothesis. Similarly, there was a significant positive linear relationship between IOD's DMI and amounts of OND rainfall at NyM Meteorological Station, \( r(37) = .42, p = .008 \), which led to rejection of the null hypothesis. Besides, the amounts of rainfall at both stations were highly correlated during a period from October to December, \( r(35) = .71, p < .001 \).

It is worth pointing out, for example, that high amounts of rain, 400 and 596 mm, were recorded at Same Meteorological Station from October to December during positive IOD phases in 1982 and 1997 when corresponding IOD's DMI values were 0.5 and 0.7, respectively. Furthermore, lower amounts of rain, 29 and 18 mm, were recorded at the same station during negative IOD phases in 1975 and 1996 when corresponding IOD's DMI values were -0.1 and -0.2, respectively. Besides, high amounts of rain, 374 mm and 272, were recorded (during similar months) at NyM Meteorological Station during positive IOD phases in 1982 and 1997 when corresponding DMI values were 0.5 and 0.7 respectively. It should be noted that lower amounts of rain, 0, 15.7, 0, 30, and 38 mm, were recorded (during the same months) at the same station in 1998, 1999, 2000, 2003, and 2005, respectively, when DMI values ranged between 0 and 0.2.

Similarly, Ogwang et al. (2015:7) explained the influence of IOD on East African OND rainfall, hence climate variability in the region.

Positive IOD (Negative IOD) event results into flood (drought) in the region. The evolution of these phenomena can thus be keenly observed and applied in seasonal forecasting to avert the huge losses associated with extreme weather events. During wet years, the wind circulation is observed to converge in the low levels over the western Indian Ocean and diverge in the upper levels, the opposite is observed in dry years.

Indeed, prolonged periods of drought from 1973 to 1976 for Same Meteorological station (Figure 2) and from 1998 to 2005 for NyM Meteorological station (Figure 3) were largely linked to climate variability. With regard to the former, Kavishe and Mushi (1993) and Limbu (1995) explained that a severe drought of 1973 – 1975 led to crop failure in several parts of Tanzania. Indeed, the drought coupled with Government's implementation of villagization program that displaced farmers and the world's oil crisis led to severe famine, which increased importation of cereals from 12,000 tons in 1972 to 521,000 tons in 1975. Consequently, the drought prompted the Government Tanzania to launch several

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**Table 7.** Correlation matrix for IOD's DMI and rainfall at same and NyM meteorological Stations.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IOD's DMI (OND)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>OND rainfall at Same station</td>
<td>0.57**</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OND rainfall at NyM station</td>
<td>0.42**</td>
<td>0.71**</td>
</tr>
</tbody>
</table>

**Correlation is significant at the 0.01 level (2-tailed).**

---

![Figure 6. IOD's DMI, 1970 to 2015.](image)

Source of data: NOAA.
campaigns to ensure food security, including *kilimo cha kufa na kupona* (*Agriculture as a matter of life and death*).

With regard to the latter, a study conducted by Kijazi and Reason (2008) established out-of-season peak in January (for years of 1998, 2000, 2001, 2003 and 2004, hence temporary displacement of short (*Vuli*) rainy seasons from OND to NDJ (November, December, January) in the lowlands of northeastern highlands. With respect to the 2004 MAM rainy season, for instance, the onset was on the 14th pentad (period of five days) (6th to 10th March) and the cessation was on the 24th pentad (26th to 30th April), hence a shorter rainy season.

Additionally, total rainfall (169 mm) for the 2004 MAM rainy season was less than half of the normal average of 388 mm. Also, the 2004 MAM rainy season was characterized with unusual dry spells from 16th to 20th March, 6th to 10th April, and 16th to 20th March. According to Kijazi and Reason (2008), the multi-year droughts from 1998 to 2005 were associated with three atmospheric circulation patterns. Firstly, wind circulation patterns diverted atmospheric moisture away from Tanzania. Secondly, there was strong moisture flux divergence in the northeastern highlands. Thirdly, there was strong subsidence, which was linked to the eastward displacement of ascending limb of the Walker-type circulation.

Moreover, both MAM and OND rainy seasons in the study area were largely driven by the yearly double passage of ITCZ between the Equator and Tropic of Capricorn (Owiti et al., 2008; Williams and Hanan, 2011; Schmidt and Spero, 2011). In turn, the migration of ITCZ was largely driven by the intensification and relaxation of migrating Azores and Siberian anticyclones in the northern hemisphere and Mascarene and St. Helena anticyclones in the southern hemisphere.

During January when the overhead Sun was experienced near the southern hemisphere, for instance, the Mascarene and St. Helena anticyclones relatively relaxed in the southern hemisphere while the Azores and Siberian anticyclones intensified in the northern hemisphere. Consequently, the rain-bearing ITCZ was largely confined in the southern hemisphere. Conversely, during July when the overhead Sun was experienced near the northern hemisphere, the Mascarene and St. Helena anticyclones relatively intensified in the southern hemisphere while the Azores and Siberian anticyclones relaxed in the northern hemisphere. Thus, the rain-bearing ITCZ was largely confined in the northern hemisphere.

### Paleo-precipitation changes in the study area

To begin with BIT index covering a period of the last 2.2 ka, highest BIT values (> 0.8), implying wettest periods that were accompanied with floods, occurred between 650 and 950 CE, and between 1550 and 1700 CE (Figure 7). To the contrary, lowest BIT values (< 0.5), implying driest periods, occurred between 1170 and 1300 CE, and between 1780 and 1820 CE. In addition, low BIT values occurred between 1870 and 1895 CE and between 1968 and 1974 CE.

In this regard, a study conducted by Scroxton et al., (2017) reported similar wet phases between the 6th and 10th centuries and between the 16th and 18th centuries for: i) Anjohibe speleothem, Madagascar based on δ18O record, ii) Cave Defore speleothem, Oman based on δ18O record, iii) Lake Edward, Uganda/Democratic Republic of Congo based on Mg/Ca in Calcite, iv) Lake Naivasha, Kenya, based on Lake level (m), and v) Liang Luar Cave speleothem, Flores, Indonesia based on PC1. Specifically, Verschuren et al. (2000) observed an agreement between (multi-) decadal trends in Lake Challa’s varve thickness record and the 1100-year moisture-balance reconstruction from Lake Naivasha, Central Kenya.

Moreover, such state of affairs was attributed to both zonal Walker Cell dynamics controlled by the Indian Ocean and meridional shifts in the average position of ITCZ that influenced the intensity of northeasterly and southeasterly monsoons/rains. Indeed, monsoon rainfall, controlled by insolation forcing and ENSO dynamics, varied at half-processional (11,500 years) interval (Verschuren et al., 2009; Wolf et al., 2011; Buckles, 2016).

Furthermore, the driest period that occurred between 1110 and 1310 CE was partly associated with a period of high volcanic activity (the Medieval Volcanic Activity) between 1250 and 1500 CE when global temperatures cooled dramatically as explained by the theory of volcanic activity (IPCC, 2013). In addition, a study conducted by Scroxton et al.,(2017) reported similar drier periods between the 11th and 15th centuries and in the 20th century for five hydroclimate stations as mentioned above. Likewise, a study conducted by Verschuren et al. (2000) suggested the existence of drier conditions in Equatorial East Africa during the Mediaeval Warm Period (1000 to 1270 CE) and the relatively wetter conditions during the Little Ice Age (1270 – 1850) that were interrupted by severe drought episodes (1380 to 1420 CE, 1560 to 1620 CE, and 1760 to 1840 CE). Generally, such findings suggested that both zonal and meridional mechanisms controlled tropical precipitation variability during the late Holocene. It should be noted, however, that the relatively drier and windier conditions existed in Lake Malawi, within the African Rift Valley, partly due to the weakening of the Congo Basin Monsoon during the Little Ice Age (Scroxton et al., 2017).

Pertaining to the BIT index covering a period of the last 25 ka, lowest BIT values (< 0.6), implying driest periods, occurred during Heinrich 2 stadial, the late Last Glacial Maximum and early Late-glacial period (including Heinrich 1 stadial) (20.4 - 15.9 ka BP) and during the
Younger Dryas (13.1 - 11.7 ka BP) (Figure 8). In addition, drier conditions occurred during the mid Holocene (6 ka BP) and late-Holocene between 0.8 and 0.6 ka BP (ca.1100 - 1300 CE) and between 0.2 and 0.15 ka BP (ca.1750-1810 CE). Excluding Heinrich 2 stadial, wetter conditions occurred from 25 to 22 ka BP. Additionally, wetter conditions occurred from 14.5 to 8.5 ka BP (excluding the Younger Dryas) and since 4.5 ka BP to present.

Indeed, paleo-precipitation reconstruction (Figure 8) was in agreement with the reconstruction of Lake Challa’s surface levels, encompassing high stands and low stands, based on a high-resolution seismic-reflection stratigraphy survey (Moernaut et al., 2010; Buckles et al., 2016).

Besides, there was agreement of periods with drier conditions during the Younger Dryas (13.1- 11.7 ka BP) and Heinrich 1 stadial (15 – 18 ka BP) for Lake Challa area (based on BIT), Greenland composite (NGRIP-GISP2-GRIP) based on atmospheric CH4 record, Greenland (NGRIP) based on ice core δ18O with respect to GICC05 timescale, and Hulu/Dongge cave based on stalagmite δ18O (Verschuren et al., 2009). Additionally, there was agreement of a period with wetter conditions between the Younger Dryas and Heinrich 1 stadial between the four hydroclimate stations. Such findings suggest that precipitation patterns for Lake Challa area during a period of the last 25 ka was largely influenced by teleconnections of natural atmosphere-ocean modes of climate variability including IOD and ENSO and meridional shifts in the average position of ITCZ.

Moreover, a study conducted by Wolff et al. (2011) revealed that thin varves from Lake Challa highly correlated with El Niño events (positive Niño3.4 values) during a period of the previous 155 years while thick varves highly correlated with La Niña events.
Niño3.4 values). Indeed, La Niña events were associated with existence of strong winds that enhanced upwelling of nutrients and intensification of seasonal blooms of algae and, consequently, the formation of thicker varves. To the contrary, El Niño events were associated with existence of weak winds that led to the formation of thinner varves. Basing on analysis of varve structure, El Niño events with high rainfall over Lake Challa area occurred in years of 1997/98, 1982/83, 1941/42, 1914/15, 1905/06 and La Niña events with low rainfall occurred in 1988/89, 1971/72, 1955/56, 1950/51, 1924/25, 1917/18, and 1897/98.

CONCLUSIONS AND RECOMMENDATIONS

This paper sought to assess linkages between precipitation changes in semi-arid lowlands of Mwanga District and both human-induced climate change and natural modes of climate variability across different temporal scales. Since the findings revealed statistically significant decrease of annual rainfall at both Same and NyM Meteorological stations, it was concluded that the human-induced climate change had occurred in the study area between the 1970s and 2010s. Besides, the findings revealed, during the same time and stations, statistically significant correlations between amounts of rainfall (September – February) and ENSO’s Niño 3.4 index and between amounts of OND rainfall and IOD’s DMI. In this regard, it was concluded that precipitation changes during short rainy seasons (*Vulis*) in the lowlands were significantly influenced by cycles of climate variability (namely, ENSO and IOD).

Indeed, rainfall fluctuations during the last 25 ka were also influenced and shaped by meridional shifts in the average position of ITCZ and zonal Hadley/Walker Cell dynamics in the Indian Ocean due to changes in insolation forces. Furthermore, the findings revealed higher average coefficient of variation for rainfall at NyM Meteorological Station and lower average coefficient of variation for rainfall at Same Meteorological Station. In this respect, it was concluded that rainfall variability at Same Meteorological Station was lower as influenced by, among other things, topographical factors and continentality.

Since increasing rainfall perturbations pose significant risks on economic activities, including rain-fed agricultural production systems, that provide livelihoods to the majority of residents in the study area, there is a need to undertake studies aimed at enhancing synergies between traditional environmental knowledge systems (TEKS) and modern-day environmental knowledge systems (MEKS) as early warning systems. With regard to TEKS, studies could focus on traditional weather prediction through observation of changing appearance and positions of astronomical objects, such as a moon/stars (*Ngalakeri* in Pare language) and fruiting/ripening of fruits of wild plants, such as *Mikayo* (*Salvadora persica*) and *Baobab* (*Adansonia digitata*). Pertaining to MEKS, studies could focus on ways of enhancing reliability of modern weather forecasting and timely dissemination of weather advisories to stakeholders.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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