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**Changes In Microbial And Soil Organic Matter Following Amendment With Olive Mill Wastewaters**

Ali Mekki, Abdelhafidh Dhouib and Sami Sayadi

**Mixed Contaminant Interactions In Soil: Implications For Bioavailability, Risk Assessment And Remediation**

Raymond A. Wuana, Felix E. Okieimen and Rebecca N. Vesuwe

**Adequacy Of Ventilation Systems: An Explorative Study Of The Perspectives Of Designers And Occupants Of High Rise Buildings In Nairobi, Kenya**

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**Variation Of Small Scale Wetland Fishery In Relation To Land Use Along Mpologoma Riverine Marsh In Eastern Uganda**

Ssanyu Grace Asiyo, Julius Kipkemboi , Jude M. Mathooko and John Balirwa

**Seasonal Physico-Chemical And Microbiological Pollutants Of Potable Groundwater In Qena Governorate, Egypt: A Case Study**

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**Perspective Of Young Drivers Towards The Care Of The Road Traffic Injured**

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## Full Length Research Paper

# Changes in microbial and soil organic matter following amendment with olive mill wastewaters

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In this work, the occurrence of the untreated and treated olive mill wastewaters (OMW) amendment on the soil organic matter recycling and on its microbial biomass evolution were investigated. Compared to the control, soils amended with untreated and treated OMW showed high levels of organic and mineral matters. Soil amended with untreated OMW presents low levels of total and inorganic nitrogen ( $0.38 \pm 0.03$  and  $0.08 \pm 0.02$  mg g<sup>-1</sup> dry soil). Treated OMW had a little content of pollutants (COD =  $4$  g l<sup>-1</sup> ± 0.4; phenolic compounds =  $0.6$  g l<sup>-1</sup> ± 0.04) and organic matter brought by these residues was rapidly mineralized in the soil. The number of heterotrophic bacteria was increased (from  $54 \pm 5 \cdot 10^5$  CFU g<sup>-1</sup> dry soil in control soil to  $123 \pm 11 \cdot 10^5$  CFU g<sup>-1</sup> dry soil) in response of the OMW amendment, mainly following C/N ratio correction. The amendment of the soil with untreated OMW improved the soil carbon content (2.18 times higher) while the specific respiration remained very low. However, the amendment with treated OMW positively affects the soil specific respiration that increases from 6.1 in control soil to 9.75 in soil amended with treated OMW. This phenomenon was accompanied by an enhancement (from  $12 \pm 2 \cdot 10^4$  CFU g<sup>-1</sup> dry soil in control soil to  $83 \pm 5 \cdot 10^4$  CFU g<sup>-1</sup> dry soil in soil amended with OMW) of nitrifiers number, urease and ammonium oxidases activities.

**Key words:** Olive mill wastewaters, soil, organic matter, nitrifiers, mineralization.

## INTRODUCTION

Olive oil industries are of fundamental economic importance for many Mediterranean countries that account for approximately 95% of the worldwide olive oil production (Dhouib et al., 2006a). Olive mill wastewaters (OMW) are the liquid by-product generated during olive oil production (Kapellakis et al., 2006). They are characterized by the following chemical properties: a very high content of organic matter (COD between 60 and 185 g l<sup>-1</sup>; BOD<sub>5</sub> between 14 and 75 g l<sup>-1</sup>), a low pH, and high polyphenols,

potassium and phosphorus contents (Rinaldi et al., 2003). Extremely high organic load and the toxic nature of olive mill wastewaters (OMW) prevent their direct discharge into domestic wastewaters treatment systems. To solve the problems associated with these wastewaters, different disposal methods have been proposed (Sayadi and Ellouz, 1995; Paredes et al., 2000; Casa et al., 2003; Dhouib et al., 2006b). However, the most frequently used method nowadays is the direct application to agricultural

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**Table 1.** Physico-chemical characteristics of untreated and treated olive mill wastewaters.

Characteristics	Untreated OMW	Treated OMW
pH (25°C)	5.1 ± 0.2	8.2 ± 0.2
Electrical conductivity (25°C) (dS m <sup>-1</sup> )	8.9 ± 0.1	14.1 ± 0.1
Chemical oxygen demand (g l <sup>-1</sup> )	72 ± 2.8	4 ± 0.4
Biochemical oxygen demand (g l <sup>-1</sup> )	13 ± 0.9	1.8 ± 0.14
COD/BOD <sub>5</sub>	5.53 ± 0.72	2.2 ± 0.32
Salinity (g l <sup>-1</sup> )	6.75 ± 0.66	12.1 ± 1.1
Water content (g l <sup>-1</sup> )	948 ± 17.2	984 ± 19.5
Total solids (g l <sup>-1</sup> )	52 ± 2.98	15.9 ± 0.7
Ash (g l <sup>-1</sup> )	8 ± 0.43	10.15 ± 0.5
Volatile solids (g l <sup>-1</sup> )	44 ± 1.85	4.8 ± 0.22
Total organic carbon (g l <sup>-1</sup> )	25.52 ± 1.18	3.2 ± 0.12
Total nitrogen Kjeldahl (g l <sup>-1</sup> )	0.6 ± 0.06	0.21 ± 0.03
Carbon/Nitrogen	43 ± 1.8	15 ± 0.65
P (mg l <sup>-1</sup> )	36 ± 3.6	15 ± 1.1
Na (g l <sup>-1</sup> )	0.94 ± 0.09	0.86 ± 0.08
Cl (g l <sup>-1</sup> )	1.6 ± 0.15	1.3 ± 0.11
K (g l <sup>-1</sup> )	8.8 ± 0.8	5.34 ± 0.6
Ca (g l <sup>-1</sup> )	1.2 ± 0.11	3.2 ± 0.2
Fe (mg l <sup>-1</sup> )	32 ± 2.9	38.3 ± 3.3
Mg (mg l <sup>-1</sup> )	187 ± 18.8	281 ± 27.1
Ortho-diphenols (g l <sup>-1</sup> )	9.2 ± 1.8	0.6 ± 0.04
Toxicity by LUMISTox (% I <sub>B</sub> )	99 ± 9	30 ± 2.9

soils as organic fertilizers (Fiestas and Borja, 1992; Nieto and Garrido, 1994; Mekki et al., 2006b; Mekki et al., 2007a). OMW physico-chemical composition and characteristics are well documented (Fiorentino et al., 2003; Allouche et al., 2004; Obied et al., 2005). Little is known, however, of the impact of OMW on the chemical, biochemical and biological properties of soil (Aggelis et al., 2003; Mekki et al., 2007b). Indeed, the effect of OMW addition on soil organic matter cycles is one of topics that need to be addressed from an agricultural point of view.

The present work was aimed at evaluating the occurrence of untreated and treated OMW amendment on the soil organic matter recycling and then on its microbial biomass evolution. The main goal is to know how much the OMW treatment application and its incubation in soil can remove its toxicity and their effects on the soil matter recycling.

## MATERIALS AND METHODS

### Untreated OMW origin

Untreated olive mill wastewater was taken from a three-phase discontinuous extraction factory located in Sfax, Tunisia.

### Treatment of untreated OMW

The treated OMW was obtained with an integrated process based

on aerobic fungal pre-treatment using *Phanerochaete chrysosporium* DSMZ 6909 followed by a decantation step then anaerobic digestion (Sayadi and Ellouz, 1995). The characteristics of the treated and untreated OMW are given in Table 1.

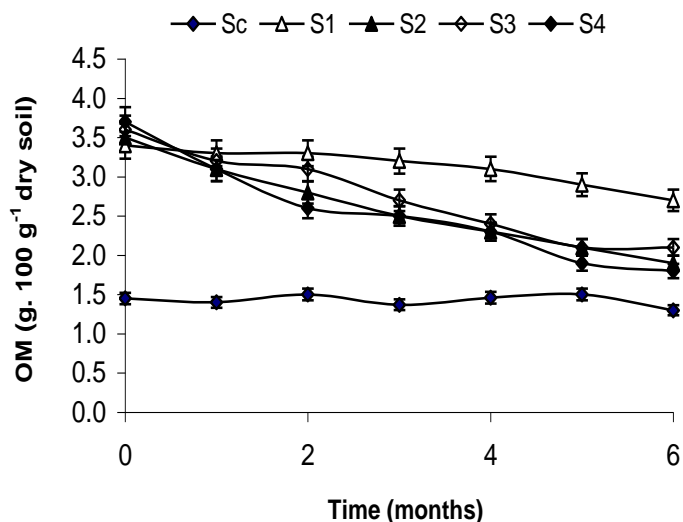
### Physico-chemical analyses

The pH and the electrical conductivity were determined according to Sierra et al. (2001) standard method. Organic matter (OM) was determined by combustion of the samples in a furnace at 550°C for 4 h. Total organic carbon was determined by dry combustion (TOC Analyser multi N/C 1000). Total nitrogen was determined by Kjeldahl method (1883). Chemical oxygen demand (COD) was determined according to Knechtel method (1978). Five-day biochemical oxygen demand (BOD<sub>5</sub>) was determined by the manometric method with a respirometer (BSB-Controller Model 620 T WTW) and phenolic compounds (ortho-diphenols) were quantified by means of Folin-Ciocalteu colorimetric method using caffeic acid as standard (Box, 1983). The absorbance was determined at  $\lambda = 765$  nm.

### Study sites and sampling

The soil of the study area was described in a previous study (Mekki et al., 2006 a). The field was divided in 5 plots. S<sub>1</sub> and S<sub>2</sub> were amended with 100 m<sup>3</sup> ha<sup>-1</sup> of untreated OMW. The amendment is achieved without (S<sub>1</sub>) or after (S<sub>2</sub>) correction of the C/N/P ratio to 100/10/1. S<sub>3</sub> and S<sub>4</sub> were amended with 400 m<sup>3</sup> ha<sup>-1</sup> of treated OMW. The amendment is achieved without (S<sub>3</sub>) or after (S<sub>4</sub>) correction of the C/N/P ratio to 100/10/1. The fifth plot, plot S<sub>c</sub>, was not amended and served as a control.

Amendment was realized in February 2006. Soil samples (S<sub>1</sub>, S<sub>2</sub>,



**Figure 1.** Soil organic matter evolution as a function of amended OMW and time.

S<sub>3</sub>, S<sub>4</sub> and S<sub>c</sub>) were collected monthly (during 6 months) from different parts of each plot from 0 to 20 cm deep, using a soil auger. All soil samples, taken from each plot were then mixed, air-dried, sieved with a mesh size of 450  $\mu\text{m}$  and stored at 4°C prior to use. Water content was immediately determined before air-drying the sample.

#### Physico-chemical soils analyses

pH and electrical conductivity were determined according to Sierra et al. (2001) standard method. Organic matter was determined after furnacing samples at 550°C for 4 h. Total nitrogen was determined by the Kjeldahl method (1883). Inorganic nitrogen was determined by the Kandeler method (1995). Organic nitrogen is determined by difference between total and inorganic nitrogen.

#### Biological soil analyses

10 g of each soil sample was suspended in an erlenmeyer flask containing 90 ml of a sterile solution (0.2% of sodium polyphosphate ( $\text{NaPO}_3$ )<sub>n</sub> in distilled water, pH 7.0). The flask was shaken at 200 rpm for 2 h. Serial 10-fold dilutions of the samples in a 0.85% NaCl solution were plated in triplicate on PCA at 30°C for total bacterial counts. Nitrifiers and denitrifiers microorganisms were enumerated by the most probable number (MPN) procedure (Trolldenier, 1995). The soil biological activity was achieved by measuring respirometric evolution in the aerobic condition (Öhlinger, 1995). Urease and ammonium oxidases activities were determined according to Kandeler et al. (1999).

#### Statistical analysis

For physico-chemical analyses, three replications were used for each parameter. For biological soils analyses, each soil sample was analysed in duplicate and the dilution series were plated in triplicate for each medium. Data were analysed using the ANOVA procedure. Variance and standard deviation were determined using Genstat 5 (second edition for windows).

## RESULTS AND DISCUSSION

### Treated and untreated OMW characteristics

The physico-chemical characteristics of untreated and treated OMW are summarized in Table 1. The high pollutant load of untreated OMW and its acidity could be observed. However, treated OMW was a slightly alkaline effluent, rich in inorganic loads such as potassium, calcium, magnesium and iron. Its content of phenolic compounds was lower than 1 g l<sup>-1</sup>, reflecting a significant reduction of its toxicity from 99%<sub>I<sub>B</sub></sub> before treatment to only 30%<sub>I<sub>B</sub></sub> after treatment application (Table 1).

### OMW impact on the physico-chemical soil parameters

Untreated and treated OMW effects on some soil physico-chemical parameters such as pH, electrical conductivity (EC), organic matter (OM), soil nitrogen and soil C/N ratio have been studied. Results showed that several chemical and biochemical properties of the investigated soil changed in response to the application of OMW. The addition of treated or untreated OMW with or without C/N ratio correction didn't show a significant effect on the initial soil pH. Indeed in spite of the initial untreated OMW acidity, the follow-up of this parameter during 6 months showed a weak reduction of the soil pH (0.2 units). Then, the acidity of the untreated OMW was compensated by the soil carbonate alkalinity as was shown by Sierra et al. (2001), whereas the addition of treated OMW caused a weak increase. Indeed, the alkalinity of this waste was not buffered by the soil components.

In the same way, the count of OMW induced an increase of the soil electric conductivity. This increase is proportional to the added OMW quantity. The increase of the soil Salinity could result from the main ionic species, sodium chloride and sulphate, coming from the treated or untreated OMW (Zanjari and Nejmeddine, 2001).

The studied soil is initially poor in organic matter. OMW addition improves the soil organic and mineral matters amounts. The organic matter supplement brought by 400 m<sup>3</sup> ha<sup>-1</sup> of treated OMW is comparable to the one brought by 100 m<sup>3</sup> ha<sup>-1</sup> of untreated OMW (Figure 1). The follow-up of the biodegradation kinetics of this organic matter brought by OMW shows that for the same quantity of added organic matter, soil receiving the treated OMW (S<sub>3</sub>) presents a potential of biodegradation 3 times higher than the one of soil receiving the untreated OMW (S<sub>1</sub>). The correction of the C/N ratio accelerates this biodegradation for soil irrigated with untreated OMW (S<sub>2</sub>) and show a low effect in the case of soil receiving the treated OMW (S<sub>4</sub>) (Figure 1).

The increase of organic and mineral nutrient contents may have a beneficial effect on the soil fertility. Nevertheless, the difficulty of untreated OMW organic matter biodegradation can be explained by its richness in phenolic compounds which are toxic for the soil biological

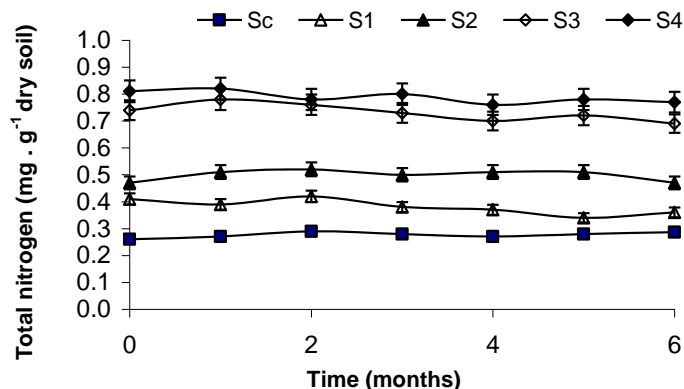


Figure 2. Soil total nitrogen evolution as a function of amended OMW and time.

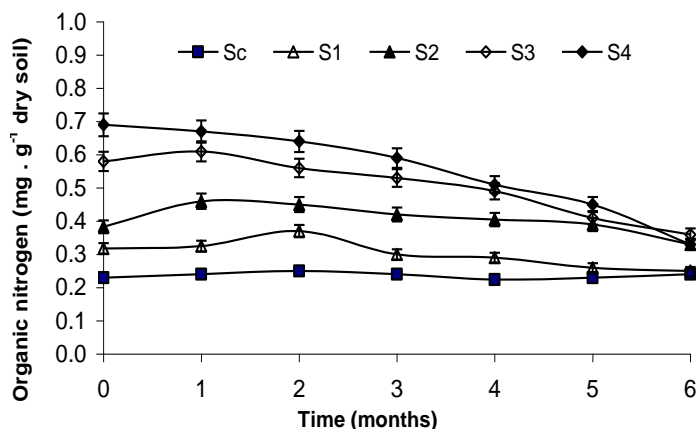


Figure 3. Soil organic nitrogen evolution as a function of amended OMW and time.

activity (Cox et al., 1998).

The OMW nitrogen content remained negligible compared to the other elements as the carbon and the potassium (Table 1). Control soil (Sc) is initially poor in nitrogen. Soil irrigated with the treated OMW presents more important total nitrogen content in that of soil receiving untreated OMW (Figure 2). The weak reduction of the total nitrogen or even its constancy during the time can be explained by the retraining of the different soil nitrogen shapes.

The organic nitrogen brought by the untreated OMW presents a slow mineralization. Indeed the affluence in suspended matters of untreated OMW enhances the immobilization of soil nitrogen. However, the organic nitrogen brought by the treated OMW turns quickly into inorganic nitrogen, what explains the important reduction of the content in organic nitrogen of soil irrigated with treated OMW (Figures 3 and 4).

The slow mineralization of the untreated OMW organic nitrogen is due to the composition of this material that facilitates its adsorption to soil particles since the untreated

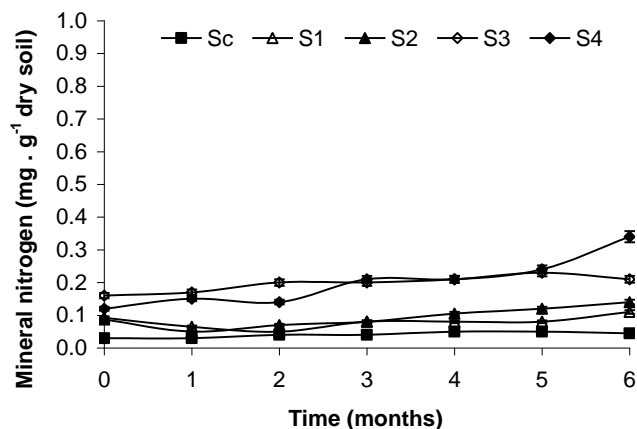


Figure 4. Soil inorganic nitrogen evolution as a function of amended OMW and time.

OMW is very rich in suspended matters. Negative effects of raw OMW on soil properties have also been recorded, including the immobilization of available nitrogen (Kissi et al., 2001).

### OMW impacts on the biological soil parameters

OMW effects on the soil aerobic heterotrophic bacteria, nitrifiers and denitrifiers microorganisms and on the soil enzymatic and respirometric activities have been studied.

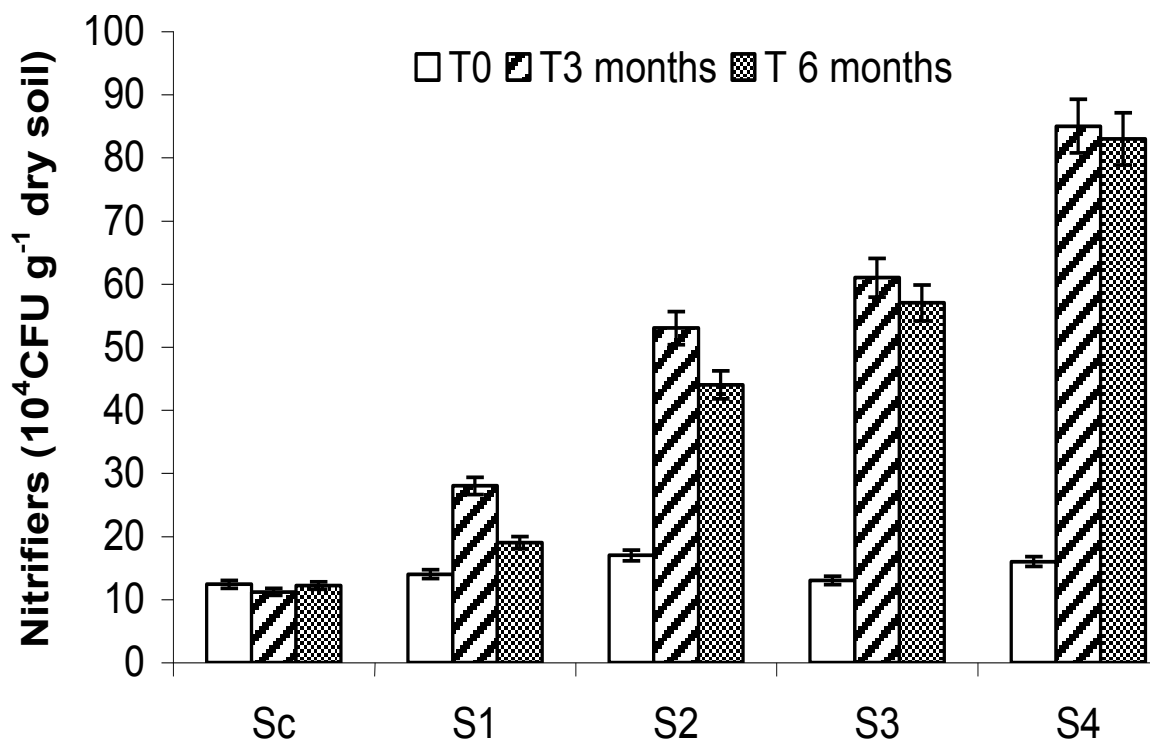
The aerobic heterotrophic bacteria counted on the studied soil are relatively weak ( $10^5$  to  $10^6$  CFU  $g^{-1}$  of dry soil). Results showed an initial increase in total number of heterotrophic bacteria after the OMW amendment, mainly following C/N ratio correction. In line with this finding, Paredes et al. (1987) reported also an increase in the total viable counts in the soil polluted with OMW (Table 2).

The control soil was very poor in organic matter and particularly in nitrogen, so the number of nitrifiers microorganisms is very weak. The OMW addition increases in a meaningful manner their number. This increase is more remarkable in the case of soil receiving treated OMW (Figure 5). However, from the 4<sup>th</sup> month after OMW addition, a reduction of these microorganisms number in all tested samples was observed. This decrease could be explained by the reduction of the soil organic nitrogen content. As it is the case for the nitrifiers, the OMW addition improves the presence of denitrifiers whose number increases correlatively with the OMW quantity (data not shown).

Indeed, nitrifiers and denitrifiers microorganisms play a critical role in the natural nitrogen cycle (Oved et al., 2001; Mendum and Hirsch, 2002). This microflora could be affected by a variety of chemical conditions including aromatic compounds and salts. The number of nitrifiers shifted from the CFU  $g^{-1}$  number ranging from 11.2 to  $12.4 \times 10^4$  in the control soil to CFU  $g^{-1}$  number ranging

**Table 2.** Aerobic heterotrophic bacteria count in the different plots and time (CFU  $10^5$  g<sup>-1</sup>).

Time (month)	March	April	May	Jun	Jul	August
Sc	54±5	49±5	52±5	49±5	50±5	51±5
S <sub>1</sub>	75±7	78±7	72±7	70±6	63±6	64±6
S <sub>2</sub>	88±8	103±9	98±8	93±9	96±9	94±8
S <sub>3</sub>	117±10	114±10	108±10	106±1	105±10	98±9
S <sub>4</sub>	123±11	126±11	117±11	109±10	111±10	107±1

**Figure 5.** Nitrifiers numbers evolution as a function of amended OMW and time.

from 13 to 61  $10^4$  in the soil amended with treated OMW. Additionally, the decomposition of OMW by soil microbes could have induced oxygen depletion in the surface soil, thereby inhibiting aerobic microbial activity (Kowalchuk et al., 2000; Schloter et al., 2003; Gianfreda et al., 2006). Besides, the OMW addition improves the presence of denitrifiers whose number increases correlatively with the OMW quantity. Indeed, these microorganisms appear more resistant to the poisonous compounds than the nitrifying bacteria.

The need to measure the activities of a large number of enzymes has been emphasized to provide information on soil microbial activity (Sukul, 2006). Urease and ammonium oxidases constitute the two major enzymes of nitrogen metabolism. Urease plays a key role in the nitrogen cycle; it contributes to the transformation of the organic nitrogen in ammoniacal assimilated nitrogen ( $N-NH_4$ ). Ammonium

oxidases assure the transformation of the product of the ammonification in assimilated nitrogen by plants ( $N-NO_3$ ) (Tscherko et al., 2003). Soils urease and ammonium oxidases activities are stimulated distinctly in soils irrigated with treated OMW, whereas the untreated OMW addition inhibits these two enzymatic activities (Table 3).

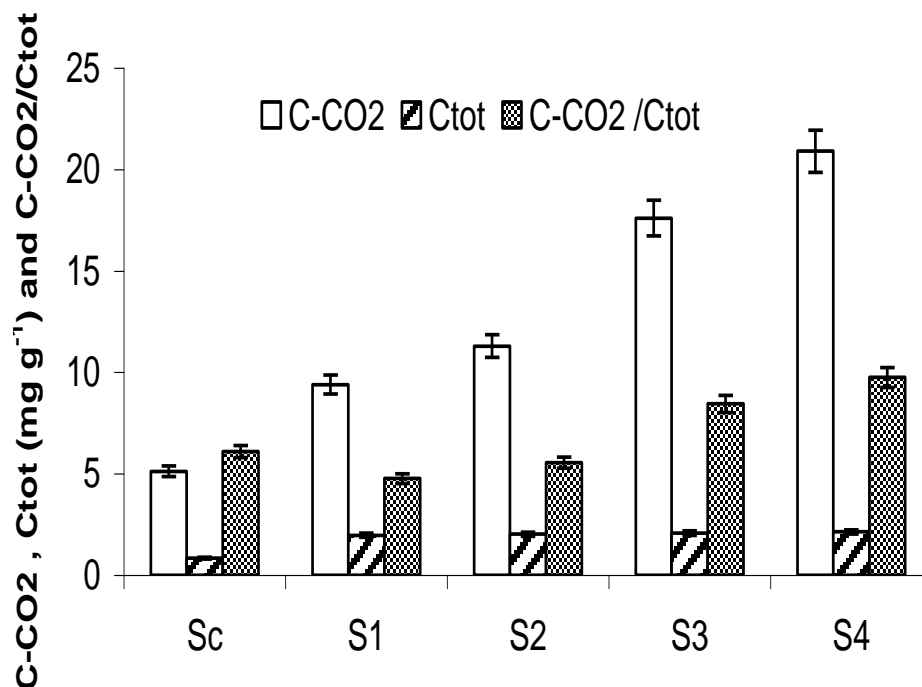
In this context, Deni and Penninckx (1999) reported that addition of hydrocarbon to an uncontaminated soil stimulated immobilization of nitrogen and reduced nitrification and soil urease activity.

The soil respirometric activity constitutes an important parameter to understand its biologic activity (Javorekova et al., 2001). A respirometric test was achieved on soils during 49 days. The specific respiration rate expressed as the ratio of  $C-CO_2/C_{tot}$  for the different soil samples is shown in Figure 6. The amendment of the soil with untreated OMW increased the carbon content while the specific



**Table 3.** Urease and ammonium oxidases activities detected in soils 6 months after OMW application.

Enzymatic activities	Urease ( $\mu\text{g NH}_4 \text{g}^{-1} 2 \text{h}^{-1}$ )	Ammonium oxidases ( $\mu\text{g NO}_2 \text{g}^{-1} 24 \text{h}^{-1}$ )
S <sub>c</sub>	30±2.8	0.22±0.02
S <sub>1</sub>	18±2	0.17±0.01
S <sub>2</sub>	29±2.5	0.21±0.02
S <sub>3</sub>	84±7	0.69±0.06
S <sub>4</sub>	98±8.2	0.89±0.07

**Figure 6.** Specific respiration  $\text{C-CO}_2/\text{C}_{\text{tot}}$ , cumulative  $\text{C-CO}_2$ , and total carbon  $\text{C}_{\text{tot}}$  of the soil samples studied.

respiration remained very low. Indeed, Rinaldi et al. (2003) reported that the affluence of the untreated OMW organic matter in toxic phenolic compounds makes difficult its biodegradation in the nature. However, the amendment of the soil with treated OMW positively affects its specific respiration. The initial correction of the C/N ratio enhances the specific respiration rate (Figure 6).

### Conclusion

Olive mill wastewaters constitute a serious environmental problem. Our results seem to confirm that the impact of OMW on soil properties was the result of opposite effects, depending on the relative amounts of beneficial and toxic organic and inorganic compounds present.

Soil organic matter recycling is assured by its autochthonous microflora. A contaminated soil constitutes an

environment limiting for the microbial normal development, and therefore an unbalance of the soil matter cycles. OMW treatment before their application on soil is therefore necessary to limit negative impact on the soil biological activity.

Treated olive mill wastewaters with white-rot fungi followed by anaerobic digestion contains again relatively high amounts of dissolved and suspended organic matter in a large volume of water and are potential candidates for use as liquid organic amendment especially for soils and crops. The use of these waters for soil amendment improves its organic pool, bring assimilated nitrogen and stimulate the organic matter mineralization.

### Conflict of Interests

The author(s) have not declared any conflict of interests.

## ACKNOWLEDGMENTS

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Review

## Mixed contaminant interactions in soil: Implications for bioavailability, risk assessment and remediation

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Majority of contaminated sites in the world contain complex mixtures of heavy metals and organic contaminants from diverse natural processes and anthropogenic activities. Mixed interactions of heavy metals and organic contaminants may affect their bioavailability and accumulation in soil and biota through synergistic or antagonistic processes. Evaluation of contaminant bioavailability is a necessary component of the overall site assessment process for establishing either bioavailability-based or risk-based, site-specific remedial options. However, contemporary approaches aimed at the effective characterisation of contaminated soils for risk assessment, remedial and regulatory purposes are frequently challenged by knowledge gaps in contaminant bioavailability, mixed contaminant effects and emerging contaminants. Understanding mixed contaminant interactions at the elemental and molecular levels is, therefore, imperative not only to explain the underlying mechanisms controlling the fate and transport of these contaminants in soils, but also predict their bioavailability, ecotoxicological effects on natural communities under realistic exposure conditions and remediation endpoints. In this paper, scattered literature is harnessed to review specific soil-contaminant interactions, inter-contaminant (metal-metal, organic-organic, metal-organic) interactions and their implications for bioavailability, risk assessment and soil remediation.

**Key words:** Heavy metals, organic contaminants, mixed contaminant interactions, co-contaminated soil, bioavailability, risk assessment, soil remediation.

### INTRODUCTION

A majority of contaminated soils in the world contain complex mixtures of heavy metals (HMs) and organic contaminants (OCs) that originate from natural processes, to some extent, and anthropogenic activities,

to a greater extent (Naidu et al., 2010; Megharaj et al., 2012). The co-occurrence of HMs and OCs in contaminated soils is an issue of great concern affecting human health and ecosystems in the world today

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(Mattson et al., 2009; Olaniran et al., 2013). Government, industry and the public are now much aware of the potential dangers that complex mixtures of xenobiotics such as HMs- mercury (Hg), cadmium (Cd), lead (Pb), nickel (Ni), copper (Cu), zinc (Zn), chromium (Cr), arsenic (As) and OCs-total petroleum hydrocarbons (TPHs), polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins and furans (PCDD/Fs), phthalic acid esters (PAEs), chlorinated solvents, pesticides, antibiotics and detergents pose to human health and the environment (Amor et al., 2001; Khan et al., 2004; Hoffman et al., 2005; Bardena et al., 2013; Yang et al., 2013). The co-occurrence of HMs and OCs in soil can adversely affect microbial processes with serious implications for biodegradation of OCs and negatively or positively affect the root growth of plants, thereby, disturbing the root enhanced dissipation of OCs (Lin et al., 2008; Couling et al., 2010; Thavamani et al., 2011a). Furthermore, mixed interactions among the HMs and OCs can synergistically or antagonistically affect their accumulation in the soil and biota (Chigbo et al., 2013). Concerns regarding the potential risks of persistent, bioaccumulative and toxic chemicals capable of long-range migration in the environment have necessitated international and national guidelines for the evaluation and control of risks posed by existing substances including HMs and OCs (Mackay and Fraser, 2000; McGrath and Semple, 2010).

The evaluation of contaminant mobility/bioavailability is a necessary component of the overall assessment of a site for establishing either mobility-/bioavailability-based or risk-based, site-specific remedial options (Nicholaidis and Shen, 2000; Ehlers and Luthy, 2003; Clothier et al., 2010). However, contemporary approaches aimed at the effective characterisation of contaminated soils for risk assessment, remedial and regulatory purposes are frequently challenged by knowledge gaps in contaminant bioavailability, mixed contaminant effects and emerging contaminants of concern (Posthuma et al., 2008; Clothier et al., 2010; Naidu et al., 2010; Pignatello et al., 2010; Clarke and Smith, 2011; Naidu and Wong, 2013). Ideas on the numerous interactions of HMs and OCs mixtures at the elemental and molecular levels are, therefore, imperative not only to explain the underlying mechanisms controlling the fate and transport of these contaminants in soils (Bertsch and Seaman, 1999), but also predict their bioavailability and ecotoxicological effects on natural communities under realistic exposure conditions (Chapman, 2002). Moreover, knowledge of mixed contaminant interactions and their antagonistic or synergistic effects in soil is required to boost soil ecotoxicological literature currently dominated by studies of single contaminant exposure (Naidu et al., 2010).

The use of models and computer simulations can significantly improve the understanding of chemical information and multi-dimensional data obtainable at contami-

nated sites (Dube et al., 2001). Despite these approaches and some investigations incorporating mixed contaminant interactions (Table 1), soil is a heterogeneous matrix whose equilibrium is shifting continually and mixed contaminant interactions are non-stereotyped and site-soil-specific. Consequently, investigations of mixed contaminant interactions continue to be necessary in tandem with global efforts to bridge the existing knowledge gaps in this aspect of environmental science. In this paper, scattered literature has been harnessed to review possible soil-contaminant and inter-contaminant (metal-metal, metal-organic, organic-organic) interactions in relation to bioavailability, risk assessment and soil remediation.

## HEAVY METAL INTERACTIONS IN SOIL

The behaviour of HMs is difficult to generalise, and so, understanding the chemistry of the particular HM and the environment of concern is necessary. However, the factors that control HM chemistry and the environmental characteristics used to produce estimates of HM fate and effects can be generalised. In natural soils, HMs exist mainly in relatively immobile forms in primary silicate minerals (for example, quartz, feldspars) and secondary clay minerals (for example, kaolinite, montmorillonite), but as a result of weathering, a fraction of the HMs content is gradually converted to mobile forms accessible to biota depending on the geological history of the area (Pierzynski et al., 2000). In contaminated soils, however, the input of HMs is mostly in non-silicate bound forms and contributes to the pool of environmentally available or bioaccessible metals the portion of total HMs in soil that is available for physical, chemical and biological modifying influences (McGeer et al., 2004). The introduction of HMs in soils through contamination eventually leads to changes in their chemical forms or phases and their multidimensional distribution, mobility and toxicity (Shiowatana et al., 2001; Buekers, 2007). The forms of HMs identifiable in soils are: (i) soil solution forms (ionic, molecular, chelated and colloidal forms) with high mobility, (ii) ions at the exchange interface, non-selectively sorbed, readily exchangeable ions in inorganic or organic fractions, (iii) ions specifically sorbed by inorganic colloids, more firmly bound ions with medium mobility, (iv) ions complexed or chelated by organic colloids, including elements present in decomposing organic materials and the soil biomass, medium to high mobility because of eventual decomposition of organic matter, (v) ions occluded by, or structural components of, secondary minerals and other inorganic compounds, medium metal mobility, (vi) elements incorporated in precipitated (hydr)oxides and insoluble salts, or fixed in crystal lattices of clay minerals, or present in the structure of primary minerals; low metal mobility, available after weathering or decomposition (Ure et al., 1993; Romić,

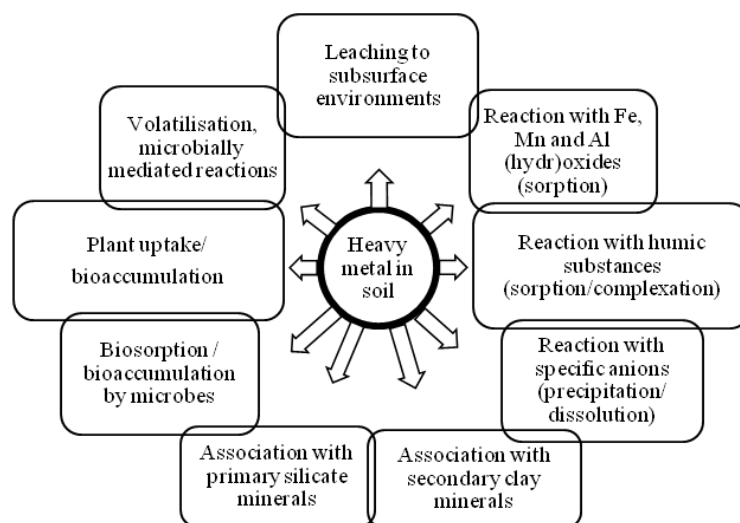
**Table 1.** Some studies incorporating mixed contaminant interactions in soil.

Contaminant	Soil texture (or type)	Location	Reference
<b>Metal-Metal</b>			
Cd, Cu, Ni, Pb, Zn	Sandy clay loam, Silty clay loam, Loam	Pamplona, Spain	Echeverría et al. (1998)
Cr, Ni, Cd	Clayey soils	Chicago, USA	Reddy et al. (2001)
Cd, Zn, Pb	Silty clay	Northern Taiwan	Lai and Chen (2005)
Cd, Cu, Cr, Pb, Zn	Sandy loam	Scotland, UK	Markiewicz-Patkowska et al.(2005)
Ni, Zn, Cu, Pb, Cd, Cr	Loamy sand, Silty loam	Olsztyn, Poland	Wyszkowska et al. (2007)
Cu, Pb, Ni, Zn		Santiago, Chile	Cazanga et al. (2008)
Cd, Pb, Ni, Cu, Zn, Co	Andisols	Agrinion, Greece	Kalavrouziotis et al. (2009)
Zn, Cd, Pb	-	Aligarh, India	Mohammad et al. (2009)
Cd, Cu, Ni, Pb, Zn	Cambisols	Makurdi, Nigeria	Wuana and Okieimen (2011)
Pb, Zn, Cd, Ni, Mn, Cu, Cr, Co, V	Sandy loam -	New Orleans, USA	Zahran et al. (2012)
<b>Metal-organic</b>			
As, Cd, Pb, Zn, Chlordane	-	New Haven, USA	Mattina et al. (2003)
As, DDT, DDD, DDE	Sand, Clay loam, Sandy clay loam	NSW, Australia	Van Zwieten et al. (2003)
Atrazine, chlorpyrifos, MMA, methylmercury	Soil/Sediment Sandy clay loam	Mississippi, USA Shanghai, China	Hwang et al. (2005) Shen et al. (2006)
Cd, Zn, Pb, PAHs	Loam	Zhejiang, China	Lin et al. (2008)
Cu, pyrene	-	Birmingham, UK	Chigbo et al. (2013)
Cd, Zn, Ni, TPHs	Loamy sand	Pretoria, SA	Atagana (2011)
Pb, Cd, Zn, Cr, Cu, As, Mn, Ni, PAHs	Sandy loam	Sydney, Australia	Thavamani et al. (2011a, b)
Cd, Pb, Zn, Cu, Mn, Co, humic acids	Fluvisol	Switzerland	Hajdu and Slaveykova (2012)
Tetracycline, Cd, Cu, Pb	Silty clays	Nanjing, China	Zhao et al. (2013)
Zn, Cu, Al, Fe, <sup>14</sup> C-phenanthrene	Sandy loam	Lancaster, UK	Obuekwe and Semple (2013)
<b>Organic-organic</b>			
TNT, pyrene	Silty loam, Loam	Maryland, USA	Chekol et al. (2002)
Phenanthrene, chrysene, dichlorobiphenyl	Sediment	The Netherlands	Morelis et al. (2007)
Surfactants, HOCs	-	-	Laha et al. (2009)
<sup>14</sup> C-PAHs	Clay loam	Lancashire, UK	Couling et al. (2010)
CBs, PAHs	-	California, USA	Faria and Young (2010)
PAHs	-	Chelsea, USA	Xiao and Huang (2011)
Fluoroquinolones, Sulfonamides	Brazilian soils	Piracicaba, Brazil	Leal et al. (2013)
Phthalate esters	Clay	Wuhan, China	Liu et al. (2013b)
TNT, RDX, HMX	Silty sand	Tennessee, USA	Sharma et al. (2013)
CBs, chloroethene	Silty sand, Silty clay	Guangzhou, China	Shu et al. (2013)
Sulfonamides	Silt loam, Clay	Hamilton, NZ	Srinivasan et al. (2013)
PAEs	Silty clay	Nanjing, China	Yang et al. (2013)

TNT = 2,4,6-trinitrotoulene ; RDX = hexahydro-1,3,5-triazine; HMX = octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine ; PAHs = polycyclic aromatic hydrocarbons; PAEs = phthalic acid esters ; POPs = persistent organic compounds; DDT = 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane; DDD = 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane; DDE = 1,1-dichloro-2,2-bis(4-chlorophenyl) ethylene; HOCs = hydrophobic organic compounds; MMA = monosodium acid methanearsonate; CBs = chlorobenzenes

2012). Evaluation of the chemical forms of HMs including free metal ions, other inorganic and organic complexes

and their associations among the soil components is referred to as chemical speciation (Ure et al., 1993;



**Figure 1.** Summary of interrelated biotic and abiotic processes determining the fate and transport of heavy metals in soils.

Templeton et al., 2000; Janssen et al., 2003; Gissera et al., 2004; Hlavay et al., 2004). The level of exposure of organisms to the HMs relative to their speciation in the soil system is called bioavailability, considered as the fraction of the contaminant's total amount that is freely available to cross an organism's cellular membrane from the soil the organism inhabits at a given time (Semple et al., 2004, 2007). In the environmental field, chemical speciation analyses can be used to accurately determine the human health or ecological risks posed by the HM species discovered and quantified at a site and redirect this understanding into the design, selection, optimization and monitoring of remediation strategies applied for site cleanup (D'amore et al., 2005). The present discourse precludes the various methods used to evaluate the speciation of HMs in solid and solution phases of soils because they have been extensively dealt with elsewhere (Tessier et al., 1979; Lake et al., 1984; Ure et al., 1993; Ma and Rao, 1997; Salbu et al., 1998; Maiz et al., 2000; Kabala and Singh, 2001; Morera et al., 2001; Filgueiras et al., 2002; Voegelin et al., 2003; Hlavay et al., 2004; D'amore et al., 2005; Zhang and Young, 2006; Rao et al., 2008; Okoro et al., 2012; Romić, 2012; Wuana et al., 2013). It, however, suffices to highlight herein, the fundamental interactions that influence the fate of HMs in soil (Figure 1).

#### **Interactions with clay minerals and Fe, Mn and Al (hydr)oxides**

Soil-HMs interactions are essentially due to the presence of a highly dispersed colloidal fraction of the soil solid phase called 'soil sorption complex' (Dube et al., 2001). In soil, HMs are loosely sorbed on alumino-silicate and phyllosilicate clay minerals as a result of the prepon-

derance of competing cations (for example, Ca). The clay minerals, however, carry Fe, Mn and Al oxides which are more effective at the adsorption of HM cations than the silicates (Violante et al., 2010). Fe and Mn oxides have a much greater adsorption capacity relative to Al oxides and other clay minerals (Basta et al., 2005). The adsorption of HM cations (for example, Pb, Cu, Zn, Cd, Cr, Hg, Ni) and oxyanions (for example,  $\text{AsO}_4^{3-}$ ,  $\text{AsO}_2^-$ ,  $\text{SeO}_4^{2-}$ ,  $\text{SeO}_3^{2-}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{WO}_4^{2-}$ ,  $\text{VO}_4^{2-}$  and  $\text{CrO}_4^{2-}$ ) onto oxide surfaces is pH dependent. The selectivity sequence of HM cation adsorption has been reported for goethite, haematite and aluminium hydroxides as:  $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Mn}$ ;  $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Mn}$  and  $\text{Cu} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Co} > \text{Cd}$ , respectively. No correlations have, however, been found between the selectivity sequences and the sequence of ionic radii ( $\text{Pb} > \text{Cd} > \text{Zn} > \text{Cu} > \text{Ni}$ ) nor between the selectivity sequences and those of electronegativity ( $\text{Cu} > \text{Pb} > \text{Ni} > \text{Cd} > \text{Zn}$ ) (Abd-Elfattah and Wada, 1981). Additionally, spectroscopic techniques such as electron spin resonance (ESR) and extended x-ray absorption fine structure spectroscopy (EXAFS) have shown that the strong bonding of Pb, Cu, Co, Cr, Mn, Ni and Zn to these oxide surfaces is due to formation of inner-sphere metal surface complexes and formation of metal hydroxide precipitate phases (Lake et al., 1984; Hettiarachchi 2003; Basta et al., 2005; Violante et al., 2010). Adsorption processes in soils have historically been described using empirical isotherm equations such as the Freundlich Langmuir, Tempkin, Toth and Dubinin-Radushkevich models (Goldberg, 2005).

#### **Interactions with soil organic matter**

In addition to Fe, Al, Mn oxides, humic substances (HSs),

a fraction of soil organic matter, are another important category of sorbents for HMs in soils. Strong adsorption on HSs occurs through the formation of HM complexes, thereby, reducing HM solubility and mobility in soil (Adriano, 2003). Evidence from molecular-scale FTIR spectroscopy has revealed that HMs form strong bonds with specific functional groups of HSs: carboxylate ( $-\text{COO}^-$ ), phenolic and sulphur-hydryl ( $-\text{SH}$ ) functional groups (Zhou et al., 2005; Erdogan et al., 2007). Adsorption of HMs on HSs increases with pH because HMs preferentially binding with ionised functional groups formed with increasing pH. Metal sorption by HSs is reduced less at lower pH than metal sorption on Fe, Mn, Al oxides (Basta et al., 2005).

The tendency of HMs towards complexation by HS ligands in soils is rationalised by the Pearson's principle, commonly referred to as the hard, soft acid and base (HSAB) principle (Pearson, 1968; Smith, 2007). The HSAB principle categorises Lewis acids and bases such that  $\text{H}^+$  and all of the metal cations of interest in soil solutions are Lewis acids, while the Lewis bases include  $\text{H}_2\text{O}$ , oxyanions ( $\text{OH}^-$ ,  $\text{COO}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ), and inorganic N, S and P electron donors. The HSAB principle indicates that hard acids ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ) tend to form complexes with hard bases ( $\text{OH}^-$ ,  $\text{COO}^-$ ), while soft acids ( $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) prefer soft bases ( $-\text{SH}$ ).

Borderline acids ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ) will form complexes with a weak or strong base (Pearson, 1968; Essington, 2004; Smith, 2007). After the HM-ligand complex formation, other ligands may compete to destabilise it and form new complexes with the HM cation (Sposito, 1994). The general order of affinity for metal cations complexed by organic matter has been reported as:  $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+}$  (Adriano et al., 2002).

### Interactions with specific anions/ligands in soil solution

The pH sensitive interactions of HMs with specific inorganic (for example,  $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{OH}^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ ) and organic (for example, citrate, oxalate, fulvate and dissolved organic carbon) ligand ions through precipitation-dissolution reactions can also affect HMs sorption processes (Bolan et al., 2003a). HM cations form sparingly soluble precipitates with phosphate ( $\text{HPO}_4^{2-}$ ), sulphides ( $\text{S}^{2-}$ ), carbonate ( $\text{CO}_3^{2-}$ ), hydroxide ( $\text{OH}^-$ ) and other anions (Lindsay, 2001). The precipitation of HMs is highly pH-dependent and increases with pH for most metal cations.

Arsenate and other HM oxyanions can form insoluble precipitates with multivalent cations including Fe, Al and Ca. The HM mineral (precipitate) formed may control the amount of HM in solution hence their mobility and availability (Basta et al., 2005). Precipitation occurs when the ionic product of the dissolved metal exceeds the solu-

bility product of that phase. In normal soils, precipitation of metals is unlikely, but in highly contaminated soils, this process can play a major role in the immobilisation of metals, especially under alkaline conditions (Bolan et al., 2010).

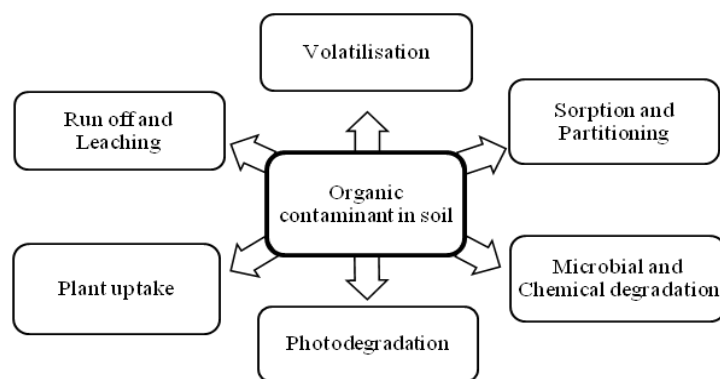
### Interactions with soil microorganisms

Soil microorganisms including bacteria and fungi can bioaccumulate HMs through either biosorption onto microbial biomass or absorption and uptake (Bolan et al., 2010). Bacteria and fungi are capable of biosorbing HMs via ion-exchange processes involving surface functional groups such as  $-\text{COO}^-$ ,  $-\text{NH}_2$ ,  $\text{OH}^-$ ,  $\text{PO}_4^{3-}$  and  $-\text{SH}$  (Srinath et al., 2002).

The affinity of HMs for the surfaces of microorganisms has been reported as:  $\text{Ni} \gg \text{Hg} > \text{As} > \text{Cu} > \text{Cd} > \text{Co} > \text{Cr} > \text{Pb}$  (Lopez et al., 2000). Soil microorganisms can also take up the HM ions and metabolically convert them into harmless forms by either precipitation or complexation. For example, *Desulphovibrio* (the sulphate reducing bacteria) releases hydrogen sulphide, precipitating the metal sulphides in the process; some bacteria produce iron-sequestering organic molecules (siderophores) in the form of phenols, catechols or hydroxamates; while some produce metal-binding proteins (metallothioneins) that serve as detoxicants (Suarez and Reyes, 2002; Cabrera et al., 2006; Bolan et al., 2010). Soil microorganisms may, however, suffer toxic effects from HMs during uptake (Wyszowska et al., 2007).

The HMs can also partake in microbially mediated oxidation-reduction reactions in soil to which, As, Cr, Hg and Se are most amenable (Bolan et al., 2010). Arsenic in soils can be oxidised to  $\text{AsO}_4^{3-}$  [As(V)] by bacteria (He and Hering, 2009). Since  $\text{AsO}_4^{3-}$  is more strongly retained than  $\text{AsO}_2^-$  [As(III)] by inorganic soil components, microbial oxidation results in the immobilisation of As. Under reducing conditions, As(III) is the dominant form of As in soils, but elemental arsenic ( $\text{As}^0$ ) and arsine ( $\text{H}_2\text{As}$ ) may also be present. As(III) is much more toxic and mobile than As(V).

In the case of Cr, the Cr(III) is strongly adsorbed onto soil particles, while Cr(VI) is only weakly adsorbed and is readily available for plant uptake and leaching into groundwater (James and Bartlett, 1983). Reduction of Cr(VI) to Cr(III) is enhanced in acidic rather than alkaline soils and can enhance the immobilisation of Cr, thereby, rendering it less bioavailable (Bolan et al., 2003b). The HMs can also be volatilised through microbial conversion to their respective metallic, hydride or methylated form. Methylation is considered to be the major process of volatilisation of As, Hg and Se in soils (and sediments), resulting in the release of the methylated forms of these elements as toxic gas (Cernansky et al., 2009). Although methylation of HMs occurs through both chemical and biological processes, biological methylation (biomethyla-



**Figure 2.** A simplified scheme of processes controlling behaviour (fate and transport) of organic contaminants in soil.

tion) is considered to be the dominant process in soils and aquatic environments (Bolan et al., 2010).

### ORGANIC CONTAMINANT INTERACTIONS IN SOIL

The fate and behaviour of OCs in soil is influenced by soil characteristics, compound properties and environmental factors such as temperature and precipitation (Reid et al., 2000). Once introduced to the soil environment, OCs may undergo volatilisation, photodegradation, or be transported by soil run-off and/or erosion to surface waters. Later on, the OCs may be leached into groundwater, and/or undergo adsorption/desorption onto/from soil inorganic/organic solid and colloidal components, partial or total chemical decomposition and/or biodegradation, and uptake by plant roots (Loffredo and Senesi, 2006; Pignatello et al., 2010). The methodological approaches used to characterise the forms, fate and transport OCs in soil have been extensively covered elsewhere (Northcott and Jones, 2000). The various processes influencing the forms, fate and transport of OCs in soil, are however, highlighted herein and summarised in Figure 2.

#### Volatilisation/leaching

The loss of OCs from soils is often biphasic, whereby a short period of rapid dissipation is followed by a longer period of contaminant release. Volatilisation and leaching are two dissipation processes of OCs in soil that exhibit similar behaviour. Volatilisation and leaching of OCs are responsible for their transfer from soil into the atmosphere and subsurface environments, respectively (Beck et al., 2009). As with the solubility, it is important to know the contribution of OC volatilisation in predicting its residual amount and thus, its persistence in the environment. The solubility of a gas dissolved in an aqueous solution is well defined by the Henry constant,  $K_H$ . For high  $K_H$  values, the molecule prefers to leave the liquid

phase in order to pass into the atmosphere. This constant is useful to describe the OC fugacity from soil solid components which are always surrounded by water in adsorbed form (Pierzynsky et al., 2000; Braschi et al., 2011). The primary rate-limiting factors governing volatilisation and leaching are postulated to be fundamental sorption/desorption mechanisms, including intra-particle diffusion, intra-sorbent diffusion and chemisorption, which control the distribution of contaminant between the solid and aqueous or gaseous phases of soils and, hence, the supply of contaminant available to the various dissipation processes (Beck et al., 2009). These are, in turn, determined by the chemical and physicochemical properties of the contaminant (vapour pressure, solubility, the structure and nature of the functional groups), concentration, soil properties (soil moisture content, porosity, density, and organic matter and clay contents, depth) and environmental factors like temperature, humidity and wind speed (Pierzynsky et al., 2000; Braschi et al., 2011).

#### Photodegradation

The photodegradation of OCs is induced by sunlight either through direct or indirect process. Direct photolysis is initiated through excitation of the OC molecule by absorption of sunlight, followed by its conversion to photoproducts. In indirect photolysis, sunlight is first absorbed by organic or inorganic chromophoric compounds present in soil, other than the OC molecule itself. These compounds (for example, clay minerals, metal oxides and hydroxides, transition-metal ions, and various fractions of HSs) may then either transfer the energy to the OC molecule (photosensitisation) or produce specific, greatly reactive, short-lived photoreactants such as the solvated electron, singlet oxygen, superoxide radical anion, peroxy and hydroxyl radicals, hydrogen peroxide and various oxireductive species, which may then react with the target OC (photoinduction) (Senesi and Loffredo, 1997; Pierzynsky et al., 2000; Braschi et al., 2011).



## Microbial degradation

Microbial degradation is one of the principal mechanisms for the attenuation of persistent OCs (for example, PAHs) in soils and is affected predominantly by contaminant bioavailability and catabolic ability of indigenous microbial populations (Reid et al., 2000). Microbial degradation is characterised by processes such as hydrolysis, oxidative coupling, hydroxylation,  $\beta$ -oxidation, epoxidation, N-dealkylation, decarboxylation, ether cleavage, aromatic ring cleavage, heterocyclic ring cleavage, sulphoxidation and several synthetic reactions (Alexander, 1999; Dec et al., 2002). Various intracellular and extracellular enzymes involved in these processes, include hydrolases, esterases, amidases, phosphatases, proteases, lyases, various phenoloxidases, oxidoreductases, mono-oxygenases and various mixed function oxidases (Dec et al., 2002). The OCs with chemical structures similar to that of HSs are usually more susceptible to microbial degradation than those having little structural resemblance to HSs. Microbial degradation of OCs in the soil may be a function of (i) the specific OC the soil has been pre-exposed to, (ii) exposure concentration, (iii) the duration and form of prior exposure and (iv) antagonistic or synergistic effects of co-contaminants. The antagonistic or synergistic effects of co-contaminants can have implications for microbial degradation in terms of biodegradation and bioremediation (Couling et al., 2010).

## Soil sorption/partitioning

Sorption is probably the most important process influencing the fate and bioavailability of OCs entering soil environments (Sun et al., 2010; Yang et al., 2013). Sorption processes are driven by forces or combinations of forces related to the bonding of the sorbing species to surfaces (enthalpy-related forces) and/or the lack of solvation of the solute in the solvent (entropy-related forces). Typical sorption-related interactions between OCs and soil include: van der Waals forces, electrostatic forces,  $\pi$ -bonding, hydrogen bonding, ligand exchange reactions, dipole-dipole interactions and chemisorptions (Gevao et al., 2000; Northcott and Jones, 2000). For apolar, nonionic, hydrophobic OCs, sorbate-sorbent interactions are relatively simple, in that sorption to soil is essentially driven by the hydrophobic effect. However, for highly polar organic compounds, sorbate-sorbent interactions are often more complex and both soil organic matter fraction and the clay mineral fraction of the soil can make significant contributions to sorption (Schwarzenbach et al., 2003; Zhang et al., 2014).

Most soil minerals, including Fe, Mn, Al (hydr)oxides, aluminosilicates (for example, allophane), clay-size layer silicates, and even primary minerals common in soil, possess catalytic properties and are able to mediate several OC transformations. For example, the surfaces of

mineral colloids behave as Brønsted acids and have the ability to protonate many uncharged OCs, and thus favour their degradation reactions by surface acid catalysis. Mineral phases also contribute markedly to the complexity of biodegradation processes by surface adsorption of microorganisms, thus altering, and drastically reducing, their biological activity and mobility (Loffredo and Senesi, 2006).

The soil organic matter content (especially the HSs fraction) influences the adsorption of OCs in soil to a large extent (Xing, 2001; Gu et al., 2000; Sun et al., 2010). HSs possess favourable attributes (aromatic/heterocyclic polydispersed skeletons with chemically reactive functional groups; very reactive organic free radical moieties with high hydrophilicity/hydrophobicity and surface activity) which permit various interactions between them and OCs with important implications for contaminant bioavailability and biotoxicity. For instance, HSs are shown to be able to: (i) modify the solubility of relatively water-insoluble, non-ionic OCs (for example, PAHs, PAEs, PCBs and *n*-alkanes), possibly by partitioning into or adsorption on HSs, or by an overall increase in solvency; (ii) exert catalytic activity in some OCs transformations and (iii) act as photosensitisers in promoting the photodegradation of some OCs (Loffredo and Senesi, 2006; Pignatello et al., 2010).

Adsorption and partitioning are probably the most important modes of interaction of OCs with HSs. The OCs can be adsorbed onto HSs through specific physical and chemical binding mechanisms and forces at varying degrees and strengths. These include ionic, hydrogen, and covalent bonding, charge-transfer or electron donor-acceptor mechanisms, dipole-dipole and van der Waals forces, ligand exchange and cation and water bridging (Gevao et al., 2000; Northcott and Jones, 2000). HSs can either "attenuate" or "facilitate" the migration of OCs in soil depending on whether the adsorption occurs on insoluble, immobile HSs such as humic acids, or on dissolved or suspended, mobile fractions such as fulvic acids. Important properties that influence adsorption/desorption include: the molecular structure; the number and type of functional groups; the size, shape, and configuration; the polarity, polarisability, and charge distribution; solubility of both HSs and OCs; and the acidic or basic or neutral, ionic or nonionic nature of the OCs. The conditions of the medium, such as pH, ionic strength, redox potential and amount of water, will also greatly influence adsorption of OCs onto HSs in soil (Loffredo and Senesi, 2006; Zhang et al., 2014). Adsorption of non-polar (hydrophobic) OCs can be better described in terms of non-specific, hydrophobic, or partitioning processes between soil, water, and the HSs organic phase. The degree of chemical partitioning of hydrophobic OCs between water and HSs as well as their toxicity can be predicted by the compound-specific orga-

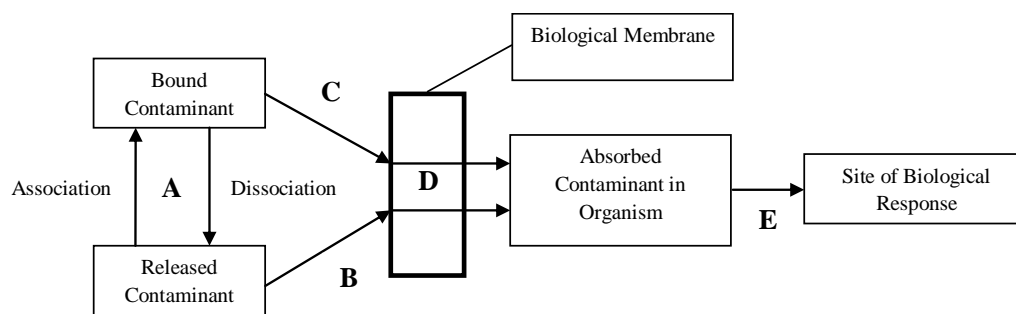


Figure 3. Bioavailability processes in soil (Ehlers and Luthy, 2003; NRC, 2003).

nic carbon normalised partition coefficient,  $K_{oc}$  (Schwarzenbach et al., 2003). The  $K_{oc}$  values for soils are largely consistent worldwide, such that  $K_{oc}$  values can serve as a sensor to assess the sorption of nonpolar OCs to the organic matter of different soils in order to save time and cost for contamination studies (Chiou and Kile, 2000). Several mechanisms of adsorption may operate simultaneously and/or in sequence for any given OC. Initially, the OC molecule may be adsorbed by HS sites providing the strongest binding (hard or glassy domain), followed by progressively weaker sites (soft or amorphous domain) as the stronger sites become filled. Once adsorbed, the OC may be subject to other processes (Loffredo and Senesi, 2006). From a toxicological perspective, binding of OCs to HS leads to: (i) a decrease of material available to interact with biota; (ii) a reduction in the toxicity of the compound; and (iii) immobilising the compound, thereby reducing its leaching and transport properties (Gevao et al., 2000). Hydrophobic partitioning is less important for polar/ionisable OCs because their retention is influenced by a complex set of physico-chemical processes, and so, it is difficult to generalise trends in their behaviour, however, their retention is more dependent on solution chemistry (especially pH and dissolved organic carbon) than is the case for nonpolar OCs (Peijnenburg and Vijver, 2007).

### IMPLICATIONS OF MIXED CONTAMINANT INTERACTIONS FOR BIOAVAILABILITY, RISK ASSESSMENT AND SOIL REMEDIATION

Mixed contaminants in the form of HMs and OCs in soil may originate from diverse natural processes (soil parent material, windblown dusts, volcanic eruptions, marine aerosols, forest fires, microbial activity) and anthropogenic activities such as agriculture (fertilisers, biosolids and animal wastes used as amendments, pesticides and irrigation water); mining and smelting (metal tailings, smelting, refining and transportation); secondary metal production and recycling operations (melting of scrap, refining, plating alloying); urban-industrial complexes (incineration of wastes and waste disposal) and auto-

mobile emissions (combustion of petroleum fuels) and emissions from power stations (Reichman, 2002; Basta et al., 2005; Wuana and Okieimen, 2011; de Souza et al., 2013).

The mixed contaminants may eventually become bioavailable to both humans and ecological receptors when exposed to them (Naidu et al., 2010). Even though ill-defined, the bioavailable contaminant may be considered as the fraction of the contaminant's total amount that is freely available to cross an organism's cellular membrane from the medium (for example, soil) the organism inhabits at a given time (Semple et al., 2004; 2007). Bioavailability of HMs and OCs in soils can be examined using a wide variety of physical, chemical and biological techniques. A comprehensive review and evaluation of these methods is provided in NRC (2003). It has been argued that the routine physico-chemical and biological techniques designed to measure the bioavailable fraction actually measure the bioaccessible fraction; defined as that which is available to cross an organism's cellular membrane from the environment, if the organism has access to the contaminant; however, it may be either physically removed from the organism or only bioavailable after a period of time (Semple et al., 2004, 2007). This methodological pitfall poses a big challenge for keying of bioavailability concept to the terrestrial regulatory framework (Naidu et al., 2010). However, it has been reasoned that measurement of the bioavailable fraction may be adopted for risk assessment purposes; while the bioaccessible fraction may be preferable when predicting remediation endpoints (Semple et al., 2007). The scheme of processes culminating in the bioavailability of contaminants in soil is illustrated in Figure 3. Figure 3A represents the release of a bound or recalcitrant contaminant to a more accessible form, B and C describe the transport of contaminant to a cellular membrane, and D represents the uptake of a contaminant across a cellular membrane (Ehlers and Luthy, 2003; NRC, 2003). Strictly speaking, process D addresses bioavailability, whereas processes A–D encompass bioaccessibility (Semple et al., 2004, 2007).

To have a physiological or toxic (hazardous) effect, the

bioavailable fraction of a contaminant has to enter the organism's cell. A risk may then be expressed as the product of contaminant toxicity (hazard) and an organism's exposure under certain doses (NEPI, 2000; Clothier et al., 2010). Knowledge of bioavailability is required for both human and ecological risk assessment to improve the accuracy of the overall risk assessment process and prioritise remedial options (Latawiec et al., 2010). In toxicity assessment, it is imperative to understand differences in contaminant bioavailability in actual populations versus a laboratory toxicity studies. Knowledge of variations in bioavailability of the contaminant in particular populations of plants and animals may also be needed to identify sensitive receptors in the population/sub-populations (NEPI, 2000); since not all species are equally susceptible to toxicants due to differences in uptake-elimination kinetics, internal sequestering mechanisms, biotransformation rates, nature or presence of biochemical receptors, rate of receptor regeneration and efficiency of repair mechanisms (Semenzin et al., 2007). Even though the level of toxicity has been quantified for many contaminants, the challenge is to quantify better the exposure pathways (Clothier et al., 2010). In exposure assessment, knowledge of bioavailability is necessary if toxicity data from one route of exposure to a contaminant is extrapolated to another route of exposure. Even within the same exposure route, differences in bioavailability will occur when mixed contaminants are present in different soils (NEPI, 2000).

Due to the great differences between the environmental behaviour of HMs and OCs (for example, OCs are subject to various abiotic and biotic degradation processes; while HMs are essentially re-distributed among various pools in soil with varying bioavailability and toxicity), it is generally becoming accepted that risk assessments for HMs should be designed differently from those for OCs. Most risk-assessment approaches have been developed for synthetic OCs (Smith, 2007), so that, for the hydrophobic OCs, a general mechanism of their toxicity is the non-polar narcotic mode of action, and it is partitioning to organic phases (measured by the compound-specific  $K_{oc}$  values) that is predominantly modulating effects (Schwarzenbach et al., 2003; Peijnenburg and Vijver, 2007). Since  $K_{oc}$  values for soils are largely consistent worldwide,  $K_{oc}$  can serve as a cost-effective sensor to assess soil contamination by OCs (Chiou and Kile, 2000). In the case of HMs, Di Toro et al. (2001) proposed a generalised framework that linked metal speciation in solution, competition of cations for binding to and accumulation on physiologically active sites (biotic ligand, BL) and ensuing toxicity responses (US EPA, 1999; Santore et al., 2001) which culminated in the biotic ligand model (BLM).

The BLM is a mechanistic-based framework in which (i) metal speciation calculations are performed, (ii) metal-organic matter interactions are accounted for by WHAM-

Model V and (iii) metal-BL interactions and resulting toxicity are established by relating critical levels of metal accumulation on the BL to dissolved metal median lethal concentration, LC50 or median lethal dose, LD50 (or other effect criteria) (Janssen et al., 2003). For mixtures of HMs and OCs in soils, any risk assessment approach must take into cognisance (i) contaminant heterogeneity across sites and interactions among co-contaminants/toxicants/stressors, (ii) complexity of soil chemistry phenomena (sorption, partitioning, speciation) with attendant effects on bioavailability/toxicity, (iii) essentiality of some HMs (for example, Cr, Cu, Ni and Zn) for plants, and (iv) differences in physicochemical characteristics of soils (van Straalen, 2002; Hund-Rinke and Kordel, 2003; Lander and Reuther, 2004; McBride, 2007). Unfortunately, contemporary literature and environmental regulatory frameworks are based on single contaminant rather than mixture effects capable of reducing or enhancing contaminant toxicity due to antagonistic or synergistic processes (Naidu et al., 2010). It is possible that contaminant mixtures do influence local ecosystems, in a site-specific way defined by all aspects along the source (local mixture)-pathway (local availability)-receptor (local species types) line, with strong possible influences of other stressors (Posthuma et al., 2008). The presence of toxicant mixtures in the field has been implicated in the differences between laboratory and field based toxicity data (laboratory-to-field dilemma) (Naidu et al., 2010).

One of the main points to consider for mixed contaminants is whether contaminants interact and produce an increased or decreased overall response as compared to the expected sum of the effects if each contaminant acts independently of each other. The interactions between different contaminants in a mixture may result in either a weaker (antagonistic) or a stronger (synergistic, potentiated) combined effect than the additive effect that would be expected from knowledge on the toxicity and mode of action of each individual compound. Interactions may take place in the toxicokinetic phase (processes of uptake, distribution, metabolism and excretion) or in the toxicodynamic phase (effects of contaminants on the receptor, cellular target or organ) (VKM, 2008; IGHRC, 2009). An additive effect occurs when the combined effect of two contaminants corresponds to the sum of the effects of each contaminant given alone.

An antagonistic effect occurs when the combined effect of two contaminants is less than the sum of the effects of each contaminant given alone (this phenomenon is well known for substances competing for the same hormonal or enzymatic receptor sites). A synergistic effect occurs when the combined effect of two contaminants is greater than the sum of the effects of each contaminant given alone (for example, the result of increased induction of metabolising enzymes when the effect is due to a metabolite).

Potentiation occurs when the toxicity of a contaminant

on a certain tissue or organ system is enhanced when given together with another contaminant that alone does not have toxic effects on the same tissue or organ system (for example, carbon tetrachloride toxicity to the liver is enhanced with isopropanol) (VKM, 2008; IGHRC, 2009). For the purpose of evaluating mixtures effects, risk assessors commonly use two simplifying toxicological models: (i) concentration addition and (ii) independent action, based on the concentration response curve of individual contaminants (VKM, 2008; Liu et al., 2013a). These models are used to classify the combined effects of contaminant mixtures as being antagonistic, additive and synergistic (also referred to as “less than additive”, “strictly additive”, and “more than additive”, respectively). Both models use contaminant concentrations in media (soil/organism) to generate concentration-response curves for individual contaminants, and these data are then used to generate specific critical concentrations for mixture models.

In the concentration addition model, all contaminants in a mixture are added together to predict toxicity; differing potencies are taken into account by converting chemical concentrations to an equitoxic dose, such as toxic units (TUs) or toxicity equivalence factors (TEFs), which convert all contaminants to one concentration. Concentration addition is often used when the constituents are known or assumed to act through the same or similar mode of toxic action. In the effects addition model, differing potencies are ignored, and the effect of each contaminant's concentration in a mixture is combined to predict mixture toxicity.

The effects addition model is used when constituents act or are assumed to act independently (different modes of action) (NEPC-EPHC, 2003; Peijnenburg and Vijver, 2007). A unifying hypothesis of mixture toxicity- the funnel hypothesis states that as the number of components in mixtures increases there is an increased tendency for the toxicity to be additive. Conversely, as the number of components decreases the tendency is for the toxicity of mixtures to increasingly deviate from additivity (NEPC-EPHC, 2003).

Consequently, a second-order polynomial model describing the effect of the different independent contaminant concentrations on toxicity can be expressed as:

$$Y = \beta_0 + \sum_{i=1}^m \beta_i X_i + \sum_{i < j} \beta_{ij} X_i X_j + \varepsilon \quad (1)$$

Where,  $Y$  is the predicted response parameter,  $X$  is the independent variable corresponding to the concentration of the different contaminants in the mixture, and  $\beta$  is the regression coefficients estimated by the stepwise regression method (Shen et al., 2006).

## Metal-metal interactions

Mixtures of HMs metals are commonly encountered in soil environments due to the wide range of soil characteristics and various forms by which HMs can be added to soil. In typical soil solution, there may be 10 - 20 different metal cations that can react with as many different inorganic and organic ligands to form 300 to 400 soluble complexes and up to 80 solid phases (Thavamani et al., 2011a). Naturally, HMs occurs in specific mineralogical associations in soil due to chemical and physical similarities of various elements. For instance, Zn ores contain significant amounts of Pb and Cd, while As is often associated with Au or Cu ores, such that one element by itself is rarely the source of contamination (Naidu et al., 2010; Zovko and Romić, 2012). Additionally, many divalent metal cations (for example,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ ) are structurally very similar and the tetrahedral structures of oxyanions such as  $CrO_4^{2-}$  and  $AsO_4^{3-}$  resemble those of  $SO_4^{2-}$  and  $PO_4^{3-}$ , respectively (de Souza et al., 2013; Olaniran et al., 2013). Due to their structural similarities, competitive interactions occur between HMs which can strongly affect their sorption onto soil solid surfaces.

Fontes et al. (2000) and Fontes and Gomes (2003) found that competition strongly influences the adsorptive capacity and mobility of metals, modifying the fitting of adsorption models. In general, the Langmuir model gives the best fit to adsorption data. Gomes et al. (2001) reported a  $Cr > Pb > Cu > Cd > Zn > Ni$  selectivity sequences. Fontes and Gomes (2003) found that in competitive adsorption some metals such as Cr, Cu, and Pb maintain their strong affinity with the surface, while others such as Ni, Zn and Cd were displaced from the surface. Competitive sorption isotherms of Cd, Cu, Ni, Pb and Zn as a function of pH for two soils, revealed that competition was enhanced as the initial metal concentration increased with approximate sequence of metal affinity for both soils being:  $Pb > Cu > Ni \geq Cd \approx Zn$  (Basta and Tabatabai, 1992). The competitive sorption of Cd, Cu, Ni, Pb and Zn on three soils studied through fractional factorial design confirmed that the presence of the competing cations reduced the amount of the five metals retained, but the presence of Cu and Pb in the system depressed Ni, Cd and Zn sorption more than the inverse (Echeverría et al., 1998). Markiewicz-Patkowska et al. (2005) also observed that the adsorption of Cd, Cu, Cr, Pb and Zn on a sandy loam was more effective in the single-element than under multi-element conditions due to competitive effects. Multi-element adsorption processes in soils can be described most conveniently using the Freundlich and Langmuir multi-component models (Goldberg, 2005).

It has been demonstrated that competitive interactions between HMs may either increase or decrease significantly the level of each other depending on whether the

interactions are synergistic or antagonistic. Synergism implies that increasing the level of one of the interacting element increases the level of the other (more than additive), while antagonism implies the converse (less than additive). Synergism particularly may have serious implications in the context of HMs contamination since it may increase the level and bioavailability of toxic elements, thereby affecting risk assessment and remediation endpoints (Kalavrouziotis et al., 2009).

Investigations of forty binary interactions of Cd, Pb, Ni, Cu, Zn and Co in soil revealed either 'one-way' or 'two-way' synergistic metal-metal interactions. A 'one-way' synergistic interaction implies that only the increase or decrease of one of the interacting elements increases or decreases the level of the other one; whereas a 'two-way' synergistic interactions means that an increase in the level of one of the interacting elements results in the increase of the other, and vice versa (Kalavrouziotis et al., 2008; Kalavrouziotis et al., 2009). The presence of co-contaminants (Cr, Cd, Ni) in kaolin and glacial till retarded the electrokinetic migration and removal of Ni and Cr in both soils due to synergistic increase in the concentration of ions in the system (Reddy et al., 2001). In soils receiving various single or mixed (binary, ternary, quaternary, quinary and sexternary) treatments of Ni, Zn, Cu, Pb, Cd, Cr, NiZn, NiCu, NiPb, NiCd, NiCr, NiZnCu, NiZnPb, NiZnCd, NiZnCr, NiZnCuPb, NiZnCuCd, NiZnCuCr, NiZnCuPbCd, NiZnCuPbCr, NiZnCuPbCdCr; Wyszowska et al. (2007) noted significant decreases in oat yield and growth inhibition of *Azotobacter* spp. upon concurrent metal application. The greatest changes in oat yield occurred when Cr was applied alone, and with Ni applied in combination with two other metals (ternary mixtures), especially when oat was grown on lighter soil. An inverse relationship has also been reported between the level of mixed metal (Pb, Zn, Cd, Ni, Mn, Cu, Cr, Co and V) contamination in community soils and school children performance in standardised tests, implying the synergistic nature of the metal-metal interactions (Zahran et al., 2012).

At the soil solution-(biological) membrane interface, the reduction in the bioavailability of undesirable HMs through competition with high concentrations of competing ions may be beneficial to crop quality but has negative implications for phytoremediation. For instance, at the root interface, inhibition of uptake of one HM another in the presence of competing cations (e.g., Ni, Cu, and Zn) has been reported (Clarkson and Luttge, 1989). There also exists, evidence of an antagonistic interaction between Zn and Cd, with Zn additions to Zn-deficient soil leading to a reduction in the Cd content of wheat and young lettuce and spinach leaves (Oliver et al., 1999), young lettuce and spinach leaves (McKenna et al., 1993) and tomato plants (Mohammad et al., 2009). Cadmium and Zn appear to compete for certain organic ligands *in vivo*, Cd competes with Zn in forming protein

complexes through antagonistic association between the two metals (Thavamani et al., 2011a).

### Metal-organic contaminant interactions

In co-contaminated soils, the transport of HMs may be enhanced in the presence of OCs due to: (i) facilitated transport caused by metal association with mobile colloidal size particles, (ii) formation of metal organic and inorganic complexes that do not adsorb to soil solid surfaces, (iii) competition with other constituents of waste, both organic and inorganic, for sorption sites, and (iv) decreased availability of surface sites caused by the presence of a complex waste matrix (Puls et al., 1991). For the OCs, microorganisms use them either as carbon source or transform them into nontoxic products with the assistance of various enzymes and extracellular products; however, the presence of HMs interferes with the microbial processes both physically and metabolically and may inhibit the biodegradation of OCs (Thavamani et al., 2011a). Metal toxicity depends on the bioavailable concentration and not necessarily the total metal content. It has been suggested that, typically, strongly complexed metals are less toxic to organisms than weakly complexed forms, which in turn, are less toxic to organisms than the free ions (Adriano, 2003). However, information on the concentrations of available as well as free metal species capable of inhibiting biodegradation is not available (Thavamani et al., 2011a). The development of techniques capable of reliably predicting the bioavailability of OCs to catabolically active soil microorganisms is required for predicting bioremediation rates and endpoints (Semple et al., 2007).

The presence of high concentrations of some metals can impact on the mobility and accessibility of PAHs in soil, with negative implications for the risk assessment and remediation of PAH contaminated soil. For instance, Obuekwe and Semple (2013) considered the effects of Zn, Cu, Al and Fe (50 and 500 mg kg<sup>-1</sup>) on the loss, sequential extractability (using various extractants), and biodegradation of <sup>14</sup>C-phenanthrene in soil over 63 day contact time and noted that the presence of Cu and Al (500 mg kg<sup>-1</sup>) resulted in larger amounts of <sup>14</sup>C-phenanthrene being extracted. The amounts extracted directly predicted the biodegradation of the PAH in the presence of the metals, with the exception of 500 mg kg<sup>-1</sup> Cu and Zn. Shen et al. (2006) also studied the combined effect of different levels of concentrations of HMs (Cd, Zn, Pb) and PAHs (phenanthrene, fluoranthene and benzo(a)pyrene) toward soil urease activity at different days of exposure (7-28 days) under controlled conditions and noted that the toxicity of HMs on urease activity decreased in the order Cd > Zn > Pb during the whole incubation time. Zinc interacted more easily with PAHs than Pb or Cd such that at 14 days, the interaction between Zn and phenanthrene was antagonistic, while at

21 days it was synergistic. At 28 days, the interaction between phenanthrene and fluoranthene was synergistic.

The magnitude and type of combined effects depend not only on the components but also on the concentrations of mixtures and incubation time. Zn is a major competitor for Cd and Pb sorption sites. Therefore, Cd and Pb can trigger the release of Zn to soil solution and enhance the bioavailability of zinc. The interaction between Zn and other pollutants may occur more easily than Pb and Cd (Shen et al. 2006). The complexation ability of an OC and divalent metal cations is necessary when evaluating their mobility in soils. The cosorption behaviour of tetracycline and HM ions onto three selected Chinese soils evaluated using batch adsorption experiments indicated that the presence of HM cations promoted tetracycline adsorption through an ion bridging effect in the order Cu (II) > Pb (II) > Cd (II), which is in accordance with their complexation ability with tetracycline. The addition of tetracycline affected metal adsorption differently depending on the solution pH and metal type (Zhao et al., 2013). Lin et al. (2006) reported that in soils co-contaminated with increasing doses (0 – 300 mgkg<sup>-1</sup>), of Cu and pentachlorophenol (PCP), both plant growth and microbial activity were inhibited at higher Cu and PCP concentrations. In soil with the initial PCP concentration of 50 mgkg<sup>-1</sup>, plants grew better with the increment of soil Cu level (0, 150 and 300 mgkg<sup>-1</sup>), implying that combinations of inorganic and organic pollutants sometimes exerted antagonistic toxic effects on plant growth. The observed higher PCP dissipation in soil spiked with 50 mgkg<sup>-1</sup> PCP in the presence of Cu and the less difference of PCP residual between strongly and loosely adhering soils further suggests the occurrence of Cu-PCP interaction the enhanced degradation and mass flow are two possible explanations. In copper co-contaminated soil with the initial PCP concentration of 100 mgkg<sup>-1</sup>, however, both plant growth and the microbial activity were inhibited with the increment of soil Cu level. The lowered degrading activity of microorganisms and the reduced mass flow were probably responsible for the significantly lower levels of PCP dissipation in copper co-contaminated soil (Lin et al., 2006). A negative effect of Cu-pyrene co-contamination on shoot and root dry matter and an inhibition of copper phytoextraction by *Brassica juncea* has also been reported (Chigbo et al., 2013) in which the level of pyrene was significantly decreased in planted and non-planted soils accounting for 90-94% of initial extractable concentration in soil planted with *B. juncea* and 79-84% in non-planted soil which shows that the dissipation of pyrene was enhanced with planting. Lin et al. (2008) also noted that increments of Cu level increased the residual pyrene in the planted soil, suggesting that the change of the microbial composition and microbial activity or the modified root physiology under Cu stress was unbeneficial to the dissipation of pyrene. The inhibition of Cu phytoextraction and degra-

ation of pyrene under co-contamination may reduce the viability of phytoremediation in sites containing multiple pollutants (Chigbo et al., 2013).

### Organic-organic contaminant interactions

In soils containing mixtures of OCs, competitive displacement processes between OCs may reverse their sequestration in soil during which a competing OC displaces the adsorbed OC into solution, taking its place in the soil matrix with attendant release of the formerly unavailable OC to the environment (Xing et al., 1996). The presence of mixed OCs may affect the sorption/desorption rates and the equilibrium concentration of the primary contaminant (White and Pignatello, 1999) and this may negatively impact OC transport predictions and soil remediation efforts in soils manifesting nonlinear sorption behaviour (McGinley et al., 1993). The effectiveness of a competitor in displacing a primary contaminant might be related to the physicochemical properties of the competitor. Just as for HMs, structurally similar OC molecules have been shown to display a stronger competitive effect because their interchangeability within the pore structure exhibits the greatest overlap (Ju and Young, 2004; Faria and Young, 2010). Xing and Pignatello (1998) reported the existence of competitive sorption between OCs and aromatic acids; implying that naturally occurring compounds may be capable of increasing the mobility and bioavailability of anthropogenic OCs. Faria and Young (2010) assessed the competitive effect for binary systems of 1,2-dichlorobenzene and other chlorobenzenes, by comparing the ability of each competitor to reduce sorption of the primary solute by measuring  $K_{OC}$ ; while a measure of competitor uptake was given by the volume of competitor in the solid phase (cm<sup>3</sup>/kg organic carbon) at equilibrium. Results indicated that competitors with structural properties closer to those of the primary contaminant had a competitive behaviour similar to that of primary contaminant itself (Ju and Young, 2004; Faria and Young, 2010).

The competitive effects of 1,2,4-trichlorobenzene (1,2,4-TCB) and tetrachloroethene (TCE) on the sorption of 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) by three soils/sediments from South China with different fractions of natural organic matter showed that cosolutes 1,2,4-TCB and TCE exhibited apparent competition against 1,2,4,5-TeCB in all the three soils. 1,2,4-TCB was a more effective competitor than TCE because the structure of 1,2,4-TCB is very close to that of 1,2,4,5-TeCB. Furthermore, the extent of competition depended on the rigidity of soil natural organic matter matrices (Shu et al., 2013; Baderna et al., 2013).

Couling et al. (2010) compared single- and multiple mixture systems of three <sup>14</sup>C-PAHs (naphthalene, phenanthrene and pyrene) and found that the presence of all three PAHs caused statistically significant

differences in the various biodegradation parameters (lag phases, maximum rates and cumulative extents of mineralisation). Any differences observed between the two systems often increased as the soil-contaminant contact time increased.

## CONCLUSION

A majority of contaminated sites in the world contain complex mixtures of HMs and OCs from diverse natural processes and anthropogenic activities. In the soil, OCs are subject to various biotic and abiotic degradation processes, while HMs are essentially re-distributed in various pools with varying mobility, bioavailability and toxicity. Contemporary approaches aimed at the effective characterisation of co-contaminated sites for risk assessment, remedial and regulatory purposes are frequently challenged by knowledge gaps in contaminant bioavailability coupled with mixed contaminant effects. Mixed contaminant effects arise from the synergistic or antagonistic interactions of the contaminants and are site-soil-waste specific. Since, evaluation of contaminant bioavailability is a necessary component of the overall assessment of a site for establishing either bioavailability based or risk-based, site-specific remedial options, understanding mixed contaminant interactions at the elemental and molecular levels is imperative, not only to explain the underlying mechanisms controlling the fate and transport of these contaminants in soils, but also predict their bioavailability, ecotoxicological effects on natural communities under realistic exposure conditions and remediation endpoints. This would help push back the frontiers of this aspect of environmental science which is currently dominated by investigations of single contaminant effects and exposure.

## Conflict of Interests

Authors have declared that there are no competing interests, neither are they foreseen.

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*Full Length Research Paper*

# Adequacy of ventilation systems: An explorative study of the perspectives of designers and occupants of high rise buildings in Nairobi, Kenya

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Passive ventilation systems have the potential for reduced operating costs in office buildings while maintaining ventilation rates consistent with acceptable indoor air quality. There is a surge of interest in more developed economies for passive ventilation technology but much work is needed before this potential can be realized in sub-Saharan Africa. This explorative study reviews the adoption and adequacy of alternative ventilations systems in office buildings located in the central business district (CBD) of Nairobi, Kenya. Data for the study was obtained through questionnaires and interviews with architects and office building occupants purposively sampled. Thirty four tenants and thirty two architects of these high rise buildings were selected as units of the study analysis. Analysis of their responses is presented using simple descriptive and interpretative techniques. The study concludes that installed ventilation systems rarely meet the needs of occupants and that greater flexibility in ventilation design could provide a measure of individual control of air circulation that would enhance their general comfort.

**Key words:** Office buildings, Nairobi, Kenya, ventilation systems.

## INTRODUCTION

Natural ventilation in large office spaces is becoming less fashionable in major cities in sub-Saharan Africa. Modern building designs incorporate mechanical ventilation systems with a few relying on the natural gifts of air flow. During the last two decades many contemporary high-rise office buildings within the central business district (CBD) in Nairobi, Kenya have adopted mechanical air-conditioning systems as their main form of ventilation

(Swinborne, 1998). Even though the outlay and use costs of mechanical systems are relatively expensive and unsustainable, current design practices do not seem to take these into cognizance enough to cause a change in design practices in Kenya.

Since the advent of mechanical ventilation systems in office buildings (beginning with the New York Stock Exchange in 1901), modern glass-walled multi-storey

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buildings have become commonplace. These developments altered traditional footprints, interior layouts and exterior appearances. For example, mechanical cooling freed designers from conventional methods of orientating office buildings in relation to the sun or ventilating them with operable windows. There was a marked shift away from traditional building designs based on T, H or L-shaped floor plans that were designed to allow maximum number of operable openings for natural ventilation. However, this made buildings more highly dependent on air conditioning systems to be able to function effectively. To design for natural ventilation is now more complex and involves a good understanding of aerodynamic concepts.

Rationally, the use and adequacy of mechanical ventilated systems needs to be continuously evaluated in different environments, considering that some climatic environments enjoy good air circulation for longer periods of the year. For example, it is useful to know if the initial outlay and use costs of mechanical ventilation systems are justifiable in a place like Nairobi, Kenya. This study therefore investigates the adequacy of the different ventilation systems designed for high rise office buildings within the Nairobi central business district. The investigation sought the opinions of both the users (occupants) and the architects (designers) of office buildings on their installed systems. The study focuses on office buildings because they have served as important laboratories for air conditioning advances since ages. Details of the investigation are presented in this paper with concluding remarks that could serve to change existing design practices. However before this, the paper reviews briefly, climatic conditions of the study area (Kenya) and gives brief descriptions of ventilation systems to underpin the study investigations.

## Background

Climatic conditions in Nairobi, Kenya suggest that passive ventilation systems will be suitable for its building designs. Nairobi is situated close to the equator, where differences between its climatic seasons are minimal. Sunrise and sunset do not vary significantly throughout the year, with two distinctive seasons: the wet season and dry season. The altitude makes for some chilly evenings, especially in the June/July season when the temperature could drop to 10°C, while the sunniest and warmest parts of the year are from December to March, with temperatures averaging the mid-twenties during the day. Nairobi climate is well suited to natural ventilation on account that it is endowed with reliable outdoor air ventilation rates, which is adequately admissible within office buildings, if duly harnessed (UNEP, 2007). The UNEP report evaluated Nairobi climatic suitability based on a single-zone model of natural ventilation heat transfer in office buildings and through the application of Bioclimatic Charts (UNEP, 2007).

However, contrary to the UNEP finding, a good number of office buildings located in the CBD area in Nairobi have installed air-conditioning systems. Several reasons addressed in the following paragraphs may account for this practice in spite of its suitability to natural ventilation. Chadderton (1997) articulates that mechanical ventilation systems may be installed in buildings for a variety of motives that could range from a real necessity for the systems, to aesthetic appeal. For aesthetic reasons, mechanical systems could help with marketing the building product when compared with other products. Makachia (1998) had identified an obsession for glass curtain walling as facade for most buildings in Kenya. This trend is set to continue unabated if a recent example, like the Afya House on Tom Mboya Street Nairobi, is anything to go by. Given that aesthetics is more of a subjective matter than objective, no convincing arguments can be offered to dissuade project owners and professionals from opting for mechanical systems.

Nairobi's cosmopolitan nature and orientation places it in an ambivalent position as it aspires to incorporate contemporary systems in its buildings which often conflicts with environmental considerations of human comfort at the micro level and as well as the urban macro climate. Designers in Kenya are often confronted with briefs requiring the utilization of contemporary materials in its large buildings (Makachia, 1998). In which case, products that are environmentally suitable in other geographical locations are imported and implanted with little prove of their environmental performance in Kenya. As was suggested by Rotimi and Kiptala (2012), there now exists in Nairobi a landscape whose creation, maintenance and survival depends not on natural determinants, but on technology and high energy inputs. Swinborne (1998) had suggested that the trend in high rise construction, where plot sizes are maximized (but with less heed to environmental considerations), negates sustainable design principles. Much building designs are aesthetic-oriented and built to maximize plot coverage. Through revision of planning density requirements, minimum plot sizes have been made lesser. Thus, the upscale Karen residential zone in Nairobi for example has changed from a minimum acreage of 2.5 acres to down to 0.5 acres in some parts. This has had an implication of increased building and infrastructure density. For the environment, this means an increase in use of solar absorptive and reflective materials in modern buildings and road infrastructure. Consequently absorbed radiation in these products is re-radiated as heat that warms up the entire city.

Little consideration is given to orientation, natural ventilation and spatial requirements for natural vegetation (Saateri, 1998). These buildings are completed with blind aping of aesthetics that could create ventilation problems (Swinborne, 1998). Consequently, recourse is made to mechanical ventilation systems to redress the anomalies emanating from these environmentally alien designs. However as Heiselberg (2000) suggests, the use of

centralized mechanical systems are largely wasteful and bear no reference to the specific requirements of individual occupants. Kavanaugh (2000) explains for example that in the UK, two-thirds of the total energy consumed for cooling is caused by mechanical fans. Brodrick and Westphalen (2001) have shown that significant gains (20 - 60 kWh/m<sup>2</sup> offset) are possible annually when buildings are naturally ventilated. Although these refer to situations in the UK, reverting to natural ventilation in climatically suitable locations such as Kenya, should confer more benefits. Swinborne (1998) concludes that the comfort derived from mechanical systems is short-lived, while it is difficult and costly to modify these installed systems to meet highly variable comfort requirements of occupants.

Leyten and Kurvers (2006) commenting on robustness of systems (measure by which a system lives up to its design purpose in a real life situation) conclude that mechanical systems lack robustness. Leyten and Kurvers (2006) suggest that mechanical systems lack robustness because they may be particularly sensitive to 'aberrations' in their underlying design assumptions, maintenance requirements of systems may not be feasible or simply not addressed, integration of heating (or cooling) and ventilation places conflicting demands on their operation and control, systems sensitive to the regulation of airflow rates (especially recirculation airflow rates) may not be feasible, and difficulties in understanding system operation on the part of both occupants and building operators. Therefore, the more complicated mechanical systems tend to be less robust, as compared to simpler more comprehensible systems. Importantly, they conclude that natural ventilation systems tend to rank high in terms of robustness (Leyten and Kurvers, 2006).

The actual health, comfort and productivity impacts of mechanical ventilation systems often fall short of expectations (Fisk and Rosenfeld, 1997; Fisk, 1998; Mendell et al., 1996). In comparisons of negative health symptoms of office building workers in a limited number of naturally and mechanically ventilated systems in Europe, naturally ventilated buildings reported lower symptom prevalence as compared to mechanically ventilated systems and especially air conditioned buildings (Seppänen and Fisk, 2002); though much of scientific findings provide conflicting conclusions, and the fundamental reasons behind these findings are not self-evident (Mendell and Fisk, 2007).

What seems of growing importance is adaptation in thermal comfort considerations (Nicol and Raja, 1997) which could be linked to Leyten and Kurvers' (2006) identification of system legibility or transparency as a prerequisite of robustness. If a system is transparent to the occupants of the building, the occupants can act directly to identify the causes of problems that compromise their health, comfort and productivity. If, in addition, office building occupants are offered control of these systems they will make changes to mitigate these

problems. This leads to the conclusion that natural ventilation systems that offer occupant control over ventilation rates (and solar gain) can be effectively designed for slightly larger comfort zones than commonly used mechanical systems (Conte and Fato 2000).

On the other side of the mechanical vs. natural ventilation systems debate, proponents of mechanical systems argue that natural ventilation is unreliable, and cannot be controlled. For example, natural ventilations systems may under-ventilate (resulting in overheating) or over-ventilate (resulting in unnecessary heating and energy consumption) because natural air flow/temperature cannot be controlled. Thus in line with Randall (1990) mechanical systems produce and maintain desired internal air environment, despite the variability of external/natural air conditions. Modern mechanical systems therefore are able to heat and cool, humidify and dehumidify, and respond automatically to changes in external air. Lee (1990) argues also that air-conditioning permits a sealing off from harsh external conditions that could protect against problems associated with health and comfort in buildings. This assertion is debatable and data collected in the current study on the adequacy of ventilation systems (which is presented later) should inform this debate.

While it is tempting to conclude from these arguments that natural ventilation systems can provide healthier, comfortable and productive environments, it may be more reasonable to conclude that robust natural ventilation systems may offer this advantage. There is a trend in the design of natural ventilation systems towards complexity. These complex natural ventilation systems may well prove to be less robust and thus may suffer shortcomings similar to those of the more complex mechanical ventilation systems. Beyond quantitative evaluations of health, comfort and productivity benefits that natural ventilation systems may offer, it is important to recognize that many if not most building occupants may simply prefer natural ventilation systems qualitatively. Largely for this reason alone, designers have accepted natural ventilation as one of several objectives of high quality sustainable designs. Thus natural ventilation systems have become a fundamental aspect of passive designs, which is an integrative design approach involving the use of daylight, thermal mass, insulation, and solar radiation in ventilation design (Yao et al., 2005). Passive ventilation should confer the least in operational costs, allowing much of natural elements to provide comfort requirements of occupants, and are environmentally friendly. This hybrid alternative, wherein mechanical devices are added to enhance system performance and control seems to be the rational solution to the debate.

From the foregoing, one could conclude that when human comfort is at risk, mechanical devices could be positively necessary but when conditions are such that only a degree of discomfort is in question, the use of mechanical devices could be made optional. The level of environmental controls could be reduced to social-economic conditions. A value judgment is involved in

deciding what degree of comfort is desired and at what cost. While passive ventilation is becoming more common design practice in developed economies, significant questions exist concerning current design practice in Kenya particularly Nairobi office buildings. Thus, the current study investigates the adequacy of installed ventilation systems through perspective views of designers and occupants of high rise office buildings in Nairobi, Kenya. Hoping that the results will provide information necessary to steer design practices towards one that takes advantage of the strength of both natural and mechanical systems.

## METHODOLOGY

### Study approach

The paper is based on an investigation into the adoption and adequacy of installed ventilations systems in office buildings located in the central business district (CBD) of Nairobi, Kenya. Data for the study was obtained through questionnaires and interviews with office building occupants and designers (architects) that were purposively sampled to become the units of the study analysis. The aim of the study was to provide information on the adoption and adequacy of installed ventilation systems so that improvements to design practices could be made evident.

Data was collected from 48 high rise buildings located in Nairobi CBD in 2010. Previous studies had indicated that there were 140 high-rise buildings (target population) that are over five storeys within the CBD area. The sample size (48) was determined for the tenant survey after Frankfort-Nachmias (1996) formula for sample size determination (Equation 1). Using the same formula, the number of architects to be surveyed was determined to be fifty (50). There are 152 registered architectural firms based in Nairobi, according to the list provided by the Board of Registration of Architects & Quantity Surveyors of Kenya (BORAQS).

$$n = \frac{Z^2 pqN}{e^2(N-1) + Z^2 pq} \quad (1)$$

Where N = Population size; n = sample size; p = sample population estimated to have characteristics being measured (95% confidence level of the target population assumed); q = 1 – p; e = acceptable error (e = 0.05, since the estimated should be 5% of the true value); Z = The standard normal deviate at the required confidence level = 1.96.

For the tenant surveys, one tenant for each building was purposely selected on the basis of those who could provide the best information to achieve the objectives of the study (Kumar, 2005). The criteria for their selection included tenants: whose office spaces are deeply placed within the buildings, who have ever raised complaint to the property manager with respect to their installed ventilation systems, and who have altered or modified their office ventilation systems at their own costs. For the architects, simple random sampling technique was employed for the questionnaire distribution.

Thirty four completed and usable questionnaires were received from the tenants corresponding to a 71% response rate, while 32 were received from architects (see Table 1 for the response rates). Mugenda and Mugenda (1999) had suggested that a 50% response rate is adequate for the analysis and reporting of questionnaire surveys. Simple interpretive and descriptive means of presentation (tabulation, charts and general statistics) in line with McQueen and

Knussen (2002) are used in this study so that the findings could be communicative to readers.

## RESULTS AND DISCUSSION

This section presents the results of the questionnaires and interviews to the two groups of research participants: office building occupants and architects. The results are discussed separately under the themes covered by each questionnaire survey, and thereafter a summary of the combined findings from both groups of participants is presented.

### Result of tenant survey

#### *Adequacy of ventilation systems*

The questionnaire for office building occupants within the CBD in Nairobi, covered three main themes. The first theme covered the adequacy of ventilation systems provided within the office spaces. There was a need to cluster the tenants into two groups so that the pattern of response from tenants with natural ventilation and those with mechanically ventilated systems can be determined. Therefore tenants were asked to comment on the operability of window openings within the building envelope and their adequacy in ventilating their office spaces. 35% (12) of the tenants said their windows were operable and that they relied solely on natural air circulation. The remaining 65% (22) said that their office windows were not operable because their offices were air-conditioned and therefore completely sealed from the external environment.

The 12 tenants who relied on natural ventilation were asked to comment further on the adequacy of air circulation within their office environment. Their response is given in Table 2 and it shows that 58.3% felt air circulation was adequate while 41.7% disagreed. 83.3% of this category of tenants were unaffected by power failure and ventilation system maintenance. This result could suggest that naturally ventilated office buildings within the CBD are able to harness the climatic endowment of air circulation in Nairobi. Though on closer observation, this category of tenants were not deeply placed within the office buildings. The remaining 16.7% that were deeply placed within the buildings required some mechanically-assisted ventilation to ensure adequate air circulation in the event of power outages.

Notwithstanding the benefits associated with natural ventilation, the survey found that 66.7% of the tenants desire supplementary ventilation systems, while 33.3% do not. This would suggest that the quality of air circulated naturally was inadequate and some form of mechanical aid was needed to complement natural ventilation.

Further, the 22 tenants that had mechanically ventilated office spaces were asked to comment on the adequacy of their installed ventilation systems. A summary of their

**Table 1.** Survey response rate.

Respondents	Total number posted	Response	Response rate (%)
Architects	50	32	64
Tenants	48	34	71
Total	98	66	67

**Table 2.** Tenants opinion on ventilation systems in office buildings.

Ventilation attributes	Naturally ventilated office spaces (n=12)		Mechanically ventilated office spaces (n=22)	
	Yes (%)	No (%)	Yes (%)	No (%)
Adequacy of air circulation within the office	58.3	41.7	41.2	58.8
Ventilation inadequacy during system maintenance and/or power failure	16.7	83.3	54.5	45.5
Desire to have alternative ventilation system	66.7	33.3	95.5	4.5

**Table 3.** Desired means of control of existing environment.

Environmental control types	Naturally Ventilated Office Spaces (n=12)		Mechanically Ventilated Office Spaces (n=22)	
	Yes (%)	No (%)	Yes (%)	No (%)
Using drapes or blinds	96.9	3.4	63.4	36.6
Open or close window to external environment	98.6	1.4	95.6	4.4
Using heater	60.2	39.8	80.2	19.8
Using local fan	90.3	9.7	85.3	14.7
Open or close a door to interior space	62.7	37.3	57.5	42.5

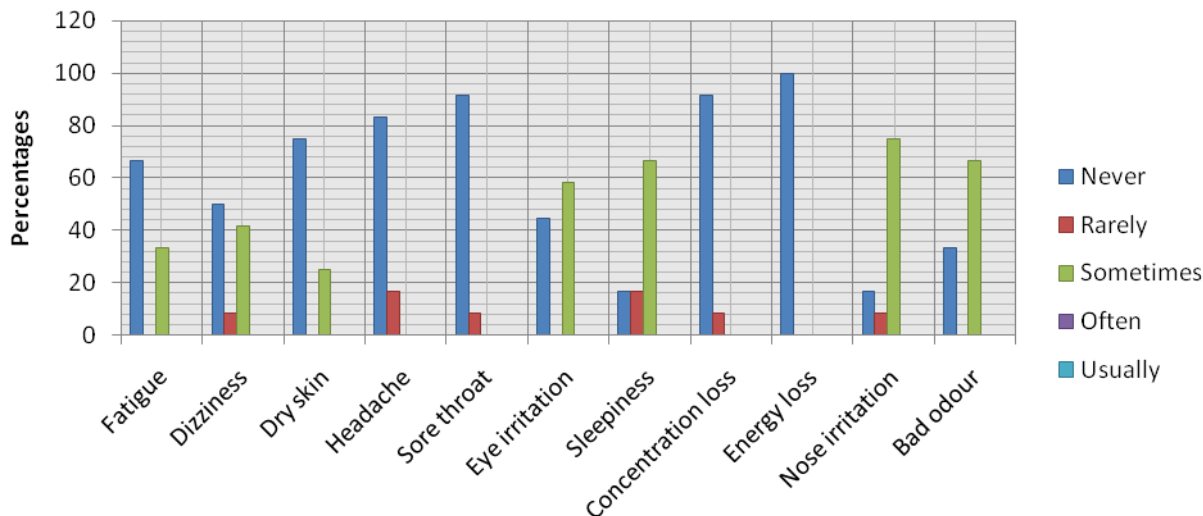
responses is given in Table 1. 41.2% of this group of tenants felt that air circulation provided by their air-conditioning systems were adequate while 58.8% had alternative views. The latter response implies that installed air-conditioning systems do not adequately meet comfort needs of these tenants. Also responding to the question relating to their personal experiences when those mechanical ventilation systems were undergoing maintenance or periods of power failure, 12 (54.5%) out of the 22 tenants confirmed that air-circulation was inadequate. The remaining 45.5% of these tenants do not experience discomfort during down periods. 95.5% of had a strong desire for alternative ventilation systems. Surprisingly tenants (45.5%) who had indicated that air circulation was adequate during power failure or shut down maintenance also desired alternative sustainable ventilation systems. Their reasons for desiring alternative ventilation systems include: the need for lower energy consuming units and to have more easily accessible units when maintenance is being carried out on the installed systems.

### **Control required for existing ventilation systems**

The second theme covered by the tenant survey is on the form of control they would like to see available for ventilation systems within their office spaces. The objective is to confirm the responses received in the first theme on the adequacy of ventilation systems in office buildings. Tenants were to indicate among a list of five alternative means by which they could improve or control air circulation within their office spaces. A summary of the results obtained from the two clusters of tenants is given in Table 3.

For tenants that rely on natural ventilation systems, there was a strong desire to control ventilation in the office spaces using all five means of control presented to them. The least was 60.2% for the use of local heating units during cold weather. While the generality of tenants would turn on a local fan to assist in cooling the office environment, or drawing the drapes or blinds to block direct sun rays into the office spaces.

For tenants occupying mechanically ventilated office



**Figure 1.** Manifestation of inadequate natural ventilation systems in office buildings

spaces, the highest percentage (95.6%) would like to be able to improve or at least control environmental conditions within their office spaces. The least percentage recorded was 57.5%, which implies overall that despite the incorporation of air-conditioning systems in office buildings, users desire some control of the internal environment (air flow and circulation) in which they operate. These results are significant to building designers as they suggest the need for wider scale consultation with end-users of office facilities so that proposed ventilation designs integrate their needs. Thus, in the event of ventilation system inefficiencies, users could be provided with options for varying the internal environment to meet their individual needs.

### **Manifestations of inadequate ventilations systems**

The last theme covered by the tenant survey was designed to give an indication of the effect of inadequate ventilation systems on the comfort of office building occupants. 11 possible effects were presented to the tenants so that they could indicate how often they experienced each of these 11 effects as a result of poor ventilation. Graphical representation of the result is presented in Figures 1 and 2 for the two clusters of respondents. For tenants occupying naturally ventilated office buildings (Figure 1), most of the manifestations, except for a few were never or rarely experienced. The exceptions include: bad odour experienced sometimes when windows were opened to promote air circulation, dizziness, nose irritation, sleepiness and eye irritation. According to the tenants, nose irritation results from cold weather which was prevalent around the month of July. This would suggest that building designs for naturally ventilated buildings have to take proper cognisance of external environmental conditions as this could affect the

quality of air within office spaces. Pollution is a key consideration in ventilation design for densely populated city centers which could manifest as poor health of building occupants.

Tenants in inadequate mechanically ventilated office buildings are affected in many ways. The different manifestations of these inadequacies are presented in Figure 2. With the exception of dry skin, concentration loss, and energy loss, which office tenants did not experience significantly, the remaining effects were significantly experienced by the tenants. In one instance, bad odour experienced within the office space was the result of dust accrual within a duct system that was not well maintained. This result suggests that buildings with installed mechanical ventilation systems need to be continuously evaluated during operation and maintained.

### **Result of architect survey**

#### **Ventilation design principles**

The results of questionnaires distributed to 32 architects based in the Nairobi area are presented in Table 4. The purpose of the questions was to determine the design considerations for ventilation systems incorporated in office buildings in Nairobi, Kenya. As observed from the table, not a convincing percentage of architects (59.4%) are aware of the suitability of Nairobi climate for passive ventilation systems. These respondents do not translate their awareness into advocacy for passive design. The response could imply that these respondents are ignorant of the fact and the issue of climatic suitability is never considered in their designs.

As is observed from the second question on Table 4, about 78% of architectural firms either rarely or never considered local weather information in ventilation



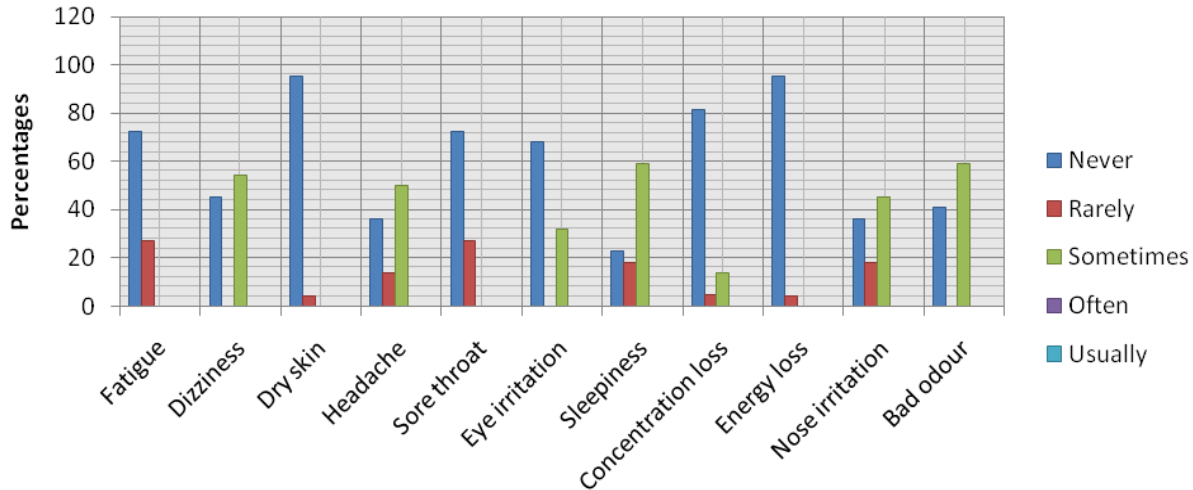


Figure 2. Manifestation of inadequate mechanical ventilation systems in office buildings.

Table 4. Design considerations for ventilations systems in office buildings.

No	Questions asked	Options	Freq	%
1	Level of awareness to climatic suitability in designing ventilation systems (n=32)	Very aware	19	59.4
		Partially aware	10	31.3
		Unaware	3	9.3
2	Extent of consideration of local weather data in ventilation design (n=32)	Never	12	37.5
		Rarely	13	40.6
		Often	7	21.8
3	Do you always consider natural ventilation during design (n=32)	Yes	23	71.9
		No	9	28.1
4	Is there relationship between building design and ventilation (n=32)	Yes	17	53.1
		No	15	46.1
5	Does natural ventilation concept affect architectural works? (n=32)	Yes	30	93.8
		No	2	6.3
6	Could the concept mentioned in qs.5 be a reason for installing mechanical systems (n=32)	Yes	26	81.3
		No	6	18.7

designs. This could explain why a high number of office buildings use mechanical ventilation over naturally ventilated systems in the Nairobi CBD. Design innovativeness would suggest that some measure of understanding and the incorporation of contextual data/information would determine their design principles. Even though responses to question 3 to 6 imply that contextual information guided the installation of mechanical systems, data obtained from the tenant surveys, suggest otherwise.

The respondents were required to indicate out of a list

of five design variables, which ones were considered the most in the design ventilation systems for office buildings. The result is presented in graphical form in Figure 3. It is observed that on aggregate ‘fashion’ seems to have been given a lot more consideration in ventilation design than ‘energy consumption efficiency’. These are followed by other design variables such as ‘maintenance’, ‘occupancy health’ and ‘orientation’ in that order. This result implies that aesthetics and fashion prevail over other design variables and also confirms the manner of responses obtained from questions 1 to 6 in Table 4.

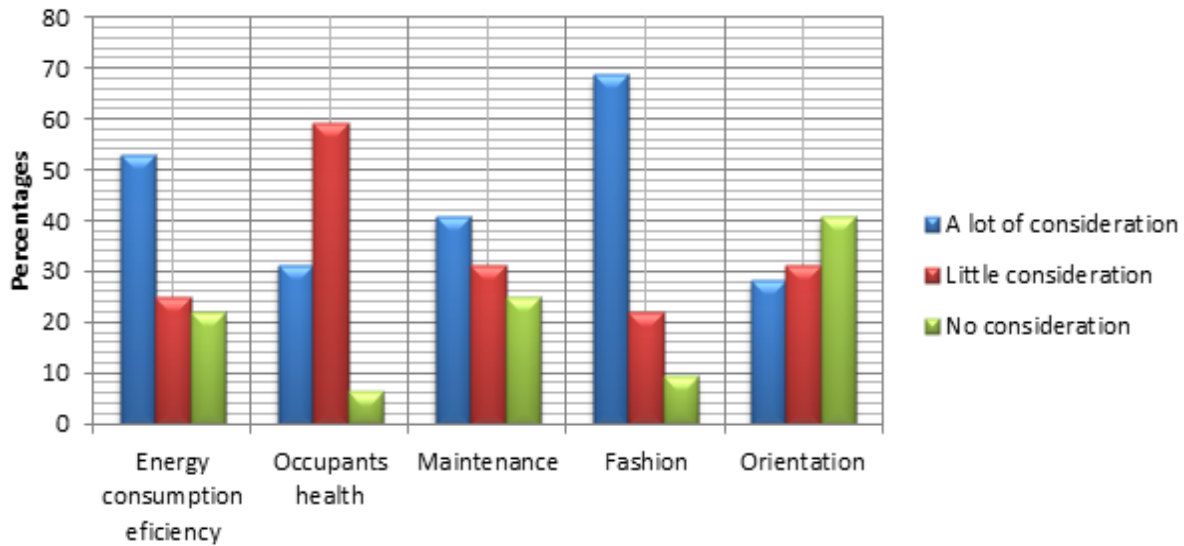


Figure 3. Consideration of design variables during ventilation design.

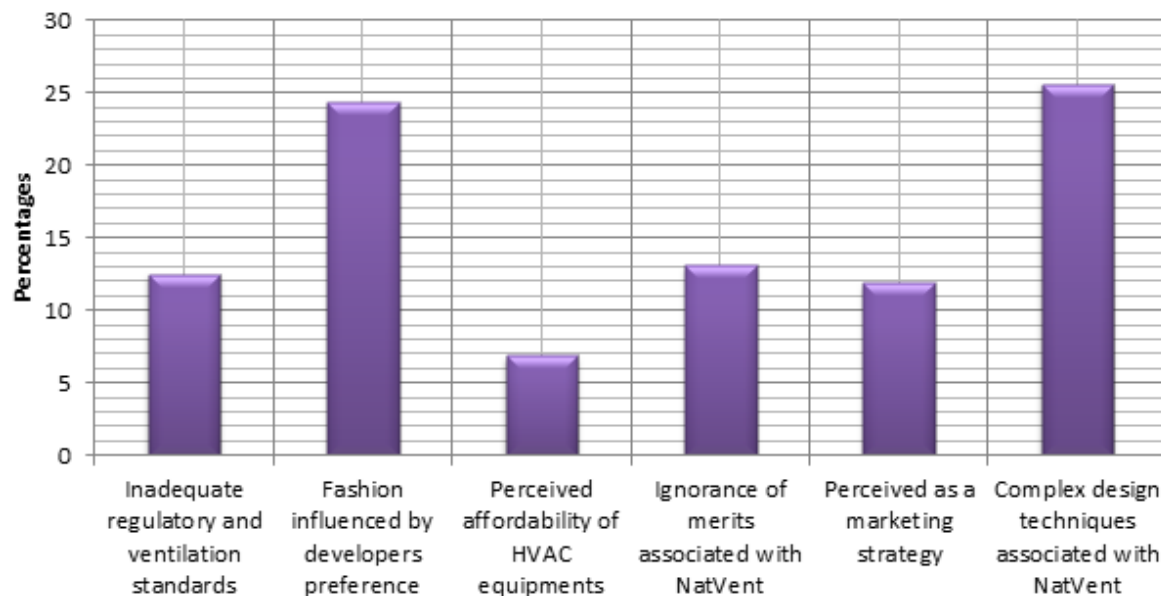


Figure 4. Reasons for mechanical ventilation systems in high rise buildings.

Further, the survey required architects to provide information on the reasoning behind mechanical ventilation systems in the CBD Nairobi, Kenya. The information gathered is presented in Figure 4. According to the architectural firms sampled, the complexities associated with designing for sustainable passive ventilation was rated the highest (25.6%) factor. Therefore, designers considered mechanical ventilations systems more because of its simplicity in design.

Following closely is developers' preferences (24.4%) for aesthetical pleasing buildings. This factor seems to

supersede designers' ventilation design options probably because developers see the installation of mechanical systems as a marketing strategy (11.9%) as well. Other important factors are the ignorance of the merits of natural ventilation (13.1%); inadequate regulatory and ventilation standards (12.5%); and affordability issues (6.9%).

On regulations and standards, some respondents express the opinion that the Local Government Adoptive Bye Laws (1968) concerning natural ventilation systems is being circumvented by designers. For example, the

bye law provides that mechanical air supply will not be required if the council is satisfied that the standard of ventilation prescribed can be maintained by natural means. However, because imported building designs with extensive glazed facades have become fashionable, mechanical ventilations systems, though expensive and unnecessary, are now inevitable fixtures in most office buildings. Further, building bye laws and regulations addressing the ventilation comfort standards in Kenya are not clear thus designers are given the carte blanche to circumvent the ventilation clause through imported or local designs that give little heed to local environmental conditions.

## Conclusion

The incorporation of mechanical ventilation systems in high-rise office buildings within the Nairobi CBD would seem from this study investigation not necessitated by unsuitable climatic conditions. The major reasons for their use are aesthetics and convenience in design practices, not necessarily its functional benefits over natural ventilation systems. Climatic conditions in Nairobi are not relatively unsuitable as would be the case in temperate regions where significant measure of control over air circulation is essential. The conclusions from this exploratory study will suggest that more consideration be given to inoperable stack effects in naturally ventilated buildings. Also in mechanically ventilated office buildings, a review of cladding materials (used on buildings facades) may be necessary so that they are compatible with the Nairobi climate.

Considerable flexibility in the design and installation of ventilation systems is highly desired by the end users as evidenced by this study. Therefore, achieving an optimum balance between both natural and mechanical systems would need to be evaluated in future designs. It was observed that tenants within the sample surveyed had installed single isolated air conditioning units because they found the central air-conditioning provided inefficient. Thus, a lot more end-user evaluation of office building designs are needed across a wide range of modern buildings. This way the benefits of an integrated approach to ventilation designs are better appreciated by end users.

Whereas this exploratory study has reached some useful conclusions, it is recommended that future work be carried out within the study area on a wider scale for the

purposes of generalizability. Also, it will be useful to capture the opinions of independent HVAC engineers on ventilation designs in Nairobi. Architects have been used in this study as proxies, though the group of architects used in the study, employed their own in-house HVAC designers in addition to their spatial design competencies.

## Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

## Variation of small scale wetland fishery in relation to land use along Mpologoma riverine marsh in Eastern Uganda

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In densely populated areas such as those in eastern Uganda where livelihoods demands create immense pressure on environmental resources, small scale wetland fisheries may be disturbed by agriculture practices. The study carried out between 2011 and 2012, investigated the variation of fish catch at the different wetland sites in relation to land use in Mpologoma riverine marsh. Four sites were identified to represent different land uses; intact wetland, minimally disturbed, highly disturbed with small scale farmers and one with a large scale irrigation scheme. Data was collected on water quality, wetland fish species catch and catch per unit effort from the different sites. Conductivity and dissolved oxygen levels significantly differed between sites and explained 72.03% of the variance among sites. Seven fish taxa dominated the wetland fishery. Large sized fish species catch, *Clarias gariepinus* and *Protopterus aethiopicus* (range of 0.45 to 38 kg/day and 0.25 to 20 kg/day respectively), was higher at the less disturbed sites than at highly disturbed sites which accounted for over 91.5% of total wetland catch. *Tilapia zillii* and *Oreochromis leucostictus* catch were also higher at the less disturbed sites while the small fish species (*Haplochromis* sp, *Clarias liocephalus* and *C. alluaudi*) did not vary with site. Conductivity and dissolved oxygen significantly correlated with the two large fish species' catch but did not correlate with small fish species catch. Agricultural activities in the wetland negatively affected the life history strategies of large fish species, leading to low catch rates at the highly disturbed site. Therefore there is need to control land use changes to secure high productivity of small scale fisheries in the riverine wetland.

**Key words:** Papyrus wetland, fish, catch, water quality, disturbance.

### INTRODUCTION

Small-scale fisheries play a significant role in human and socio-economic development and they are an entry point for poverty reduction though their role in generating revenues and creating employment, and their contribution

to food security (Heck et al., 2007; Bene et al., 2010). These are wetland fisheries which often provide a 'safety valve' for people who cannot access other sources of livelihood (Bene, 2004; 2004). The small scale wetland

fisheries provide nutritional security in remote areas that lack adequate supplies of animal protein and sustain the livelihood of landless fishers who can no longer survive by fishing in depleted freshwater bodies (Vass et al., 2009). Although wetlands provide habitat for 40% of all fish species (Arthington et al., 2004), 20% of their biota are amongst the most threatened components of global biodiversity (Smith et al., 2005). This is largely due to human induced environmental degradation. The demand for increased food production to cater for the rising human population and large numbers of undernourished or starving people, especially in the developing countries (Okechi, 2004), have led to widespread conversion of wetlands into farmland. Climate variability which has emerging signals within the River Nile Basin (Di Baldassarre et al., 2011), is likely to have a profound impact on land management practices leading to more changes in land use decisions (Verburg et al., 2011). Consequently, land requirements, reclamation potential and general environmental management are affected (Carvalho et al., 2004).

Many permanently flooded wetlands are open to fishing by anyone (open access) or subject to exclusive communal or individual use rights (Garaway et al., 2006; Martin et al., 2011). Often, wetlands under exclusive access arrangements are exploited less intensely and maintain higher standing stocks of fish than open access wetlands (Lorenzen et al., 1998). The open access wetlands may also be subject to very intensive exploitation of both water and fisheries resources (Garaway et al., 2006). In eastern Uganda, over 10% of Mpologoma River wetland is under cultivation of rice, maize and vegetable to cater for food demand of the increasing population (NEMA, 2004). Simultaneously, there appears to be reduction in the large preferred fish species, *Clarias gariepinus* and *Protopterus aethiopicus* in the Lake Kyoga basin (Muhoozi, 2003). *C. gariepinus* catch reduced from more than 1600 metric tonnes in the 1980s to 1.35 metric tonnes in 2000 (Muhoozi, 2003).

Understanding the effects of land use changes on the fisheries is essential for the management of exploited wetlands (Rientjes et al., 2011). Although there are a few existing models based on observed pattern in temperate areas, scarcity of data for most tropical riverine wetlands limits prediction of the effects of human-induced perturbations on the fish assemblages and catch (Ibanez et al., 2007). Therefore Mpologoma wetland fisheries that support local communities with no access to open lake fisheries and yet it is under intensive exploitation need evaluation. The aim of the study was the assessment of the small scale fishery dynamics in relation to land use in Mpologoma river wetland. We used comparison of the

wetland fish species catch at the wetland sites with different land use patterns. It was hypothesized that the different land use at the wetland sites would affect the fish habitat though water quality variations, leading variation in the wetland fish species catch. The spatial-temporal variation of the wetland fish species catch in Mpologoma riverine wetland was expected.

## MATERIALS AND METHODS

### Study area and sampling sites

Mpologoma river wetland in Uganda (latitude 1°12' N and longitude 34°40' E) extending up to 102 km, discharges 610 million m<sup>3</sup> of water annually into Lake Kyoga complex (Ramsar, 2008). The climate is tropical with rainfall ranging between 1470 - 2300 mm in the longer wet season. The maximum temperature range is 27 – 32°C and the minimum is 16 – 18°C. This permanent wetland is dominated by papyrus (*Cyperus papyrus*) and hippo grass (*Vossia cuspidata*). The fish species of economic importance in the Lake Kyoga complex include *Clarias gariepinus*, *Protopterus aethiopicus*, *Oreochromis leucostictus*, *O. niloticus*, *Bagrus docmak*, *Rastrineobola argentea* and *Tilapia spp* (Vanden-Bossche and Bernacsek, 1990; NaFIRRI, 2007).

Using the Digital Elevation Model of the AVSwat, a map of Mpologoma river wetland with the four differently disturbed study sites was delineated (Figure 1). The main depression which is Mpologoma riverine wetland system consists of a network of small vegetated valley bottoms, fed by 38 sub-catchments. Four study sites with different levels of disturbance were selected along the wetland. Land use cover at each site was derived from Landsat ETM images of July 2011, verified by field survey data. Seven land use classes were identified in 200 hectare polygons area about each site (Table 1). Budumba and Mazuba sites were minimally disturbed with small farms at the edge of the wetland. Kapyani site was highly disturbed with small scale rice and maize farms of acreage of 2 – 6 acres inside the wetland, using low implement agriculture and rain-fed lowland systems (MAAIF, 2009). Nsango site was highly disturbed with a large scale rice scheme occupying over 3,000 hectares of the wetland. Artificial fertilisers, rainfed lowland and irrigation systems were used at the rice scheme.

### Wetland fish assemblage

Fish samples from several fishing techniques were used to determine the wetland fish species composition and fishery production. Experimental fish sampling was done with gill nets hanged in the lagoons, while traps were placed inside the wetland. Gill nets of 2, 2.5 and 3 cm mesh sizes were set in parallel in the lagoon. Ten local basket traps were randomly deployed to catch fish inside the flooded vegetation zone of the wetland. All gear were set at around 7:00 h and retrieved before 14:00 h. This was done to reduce loss of fishing gear to the local fishermen during overnight fishing. On landing, fish samples were counted, total length and weight measured, and records of the gear and effort used at every

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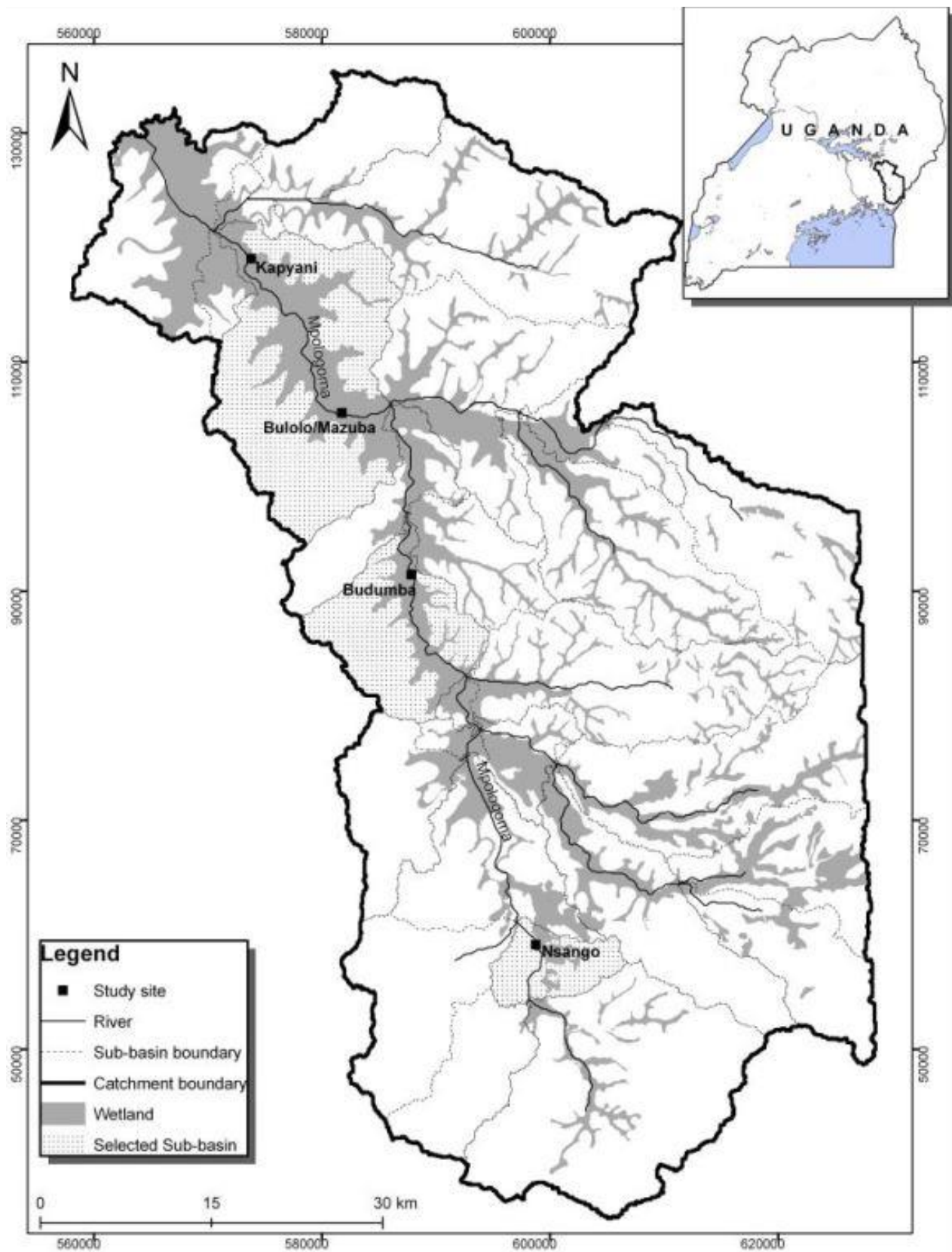


Figure 1. Location of the study sites along Mpologoma river wetland.

**Table 1.** Land use percentage cover of 200 ha area around study sites in Mpologoma River wetland, Uganda, 2011.

Land use	Mazuba	Budumba	Kapyani	Nsango
	Intact wetland	Less disturbed	Highly disturbed (with small scale farms)	Highly disturbed (Large scale rice scheme)
<b>Man made type</b>				
Built up area	0	0.48	1.52	18.13
Subsistence	0	8.67	55.25	16.18
Large scale farmland	0	0	0.00	16.16
Subtotal cover	0	9.15	56.77	50.47
<b>Natural type</b>				
Permanent wetland	100	90.63	31.21	17.30
Temporary wetland	0	0	10.15	5.58
Woodland	0	0.23	1.38	21.09
Grassland	0	0	0.48	4.31
Subtotal cover	100	90.86	43.22	48.28

site. Some fish were preserved in 40% ethanol and retained for identification using keys (Greenwood, 1974; Witte and van Densen, 1994). To cater for the seasonal changes in fishery, each site was sampled once a month for 12 months between September 2011 and August 2012.

More data on wetland fish species and catch was collected from fishermen landing catches at each site for every sampling day. The local fishermen distributed their fishing effort throughout the study site each trip to sample each portion of the study site each day. At each site, fishermen had their own culture of who fishes where, and regulated the number of fishermen per landing site. Therefore the decision of about where and how to fish was left to the fishermen. The local fishermen dominantly used gill nets (2.5 cm and 3.0 cm mesh sizes) of about 45 m long by 1.5 m deep, fishing lines with varying number of hooks and local basket traps (0.4 by 0.4 by 0.3 m, on average) as fishing gears. Fishing lines consisted of a weight (approximately 2 kg) with varying number of baited hooks mainly set to catch *Protopterus* sp. and *C. gariepinus* within the wetland. Bait materials included pieces of small fish species such as small *Clarias* species, *Tilapia* species, frogs and large insects for hooks, while dead earthworms were for basket traps. Most fishing gear were set at 18 hours and retrieved at 6:00 hours to prepare for the markets. Data on captured species brought to the landing sites were recorded including fish taxa, total length (TL, in centimeters), weight (Wt, in grams), type of gear and effort used. Total length and weight were measured as quickly as possible after the fishermen returned with their catch. For small species such as small *Clarias* sp., *Haplochromis* spp., *Tilapia* spp. and *Barbus* sp., random sub samples were taken to measure standard lengths but their total number in the catch recorded. For large species such as *C. gariepinus* and *Protopterus* sp. groups of similar sizes were counted and sub sampled for measuring their total length and weight to get as much data as possible in the limited time allowed by the fishermen.

#### Physical habitat

To characterise water quality of the wetland sites with different land uses, three water samples were collected from different points (within the wetland, middle of lagoon and edge of the lagoon) at each site. Within the wetland, three water samples were randomly collected close

to where traps were placed at each site. Conductivity and pH were determined *in-situ* using a Hanna Instruments HI 9813-6 N Waterproof pH/Ec/TDS/°C meter. Dissolved oxygen and temperature were determined *in-situ* by Oakton DO 110 meter. Chemical analysis was performed on 0.45 µm membrane filtrate for alkalinity, nitrate-nitrogen and orthophosphate and unfiltered samples for total phosphorus within 48 h of collection according to standard procedures (APHA, 1995).

#### Data analysis

Fish data were summarised into the species composition catch and catch per unit effort (CPUE) for spatial and temporal variation along the wetland. The fishermen usually fished only once a day and therefore species catch was considered as total species catch in kilogram per day. Since the fishery was a multispecies type and uses non-selective fishing gear, for gill nets and traps fishing gear, CPUE was calculated by dividing the catch in grammes of the most dominant fish species caught by the individual gear by the number of hours. Most gillnets were set for less than 5 h and most fisherman had only one net, therefore the units of CPUE of gill nets derived from the mean sizes of gillnets and fishing hours used along the wetland. Most fishermen used locally made basket traps of similar sizes and shape. Therefore the units of CPUE of traps was derived from number of traps and hours used per fisherman. CPUE of lines with hooks was calculated by dividing the catch in grammes of most dominant fish species by the hours spent in fishing considering the mean number of hooks per fisherman. Most fishermen using line hooks in the evening and check on the fish caught early morning. Therefore 12 h were used in the calculation of the hooks CPUE. Due to differences in mean number of hooks per sites, the hooks' CPUE was standardized to 100 hooks per hour. Species richness was tested using Shannon Wiener's index ( $H'$ ) of diversity (Thiebaut, 2006) in the equation;

$$H' = - \sum p_i \ln(p_i),$$

Where,  $p_i$  is the relative abundance of individual fish species.

Statistical analysis on all data was performed using SPSS version 16 (IBM ©). All the wetland fish species catch and CPUE

**Table 2.** Mean number of fishermen, fishing gear type per fisherman and boats at one major landing site of each of the differently disturbed sites along Mpologoma river wetland in 2012.

Parameter	Budumba	Mazuba	Kapyani	Nsango
Number of fishermen	22 ± 5	22 ± 4	30 ± 9	17 ± 5
Number of hooks per fisherman	85 ± 34	50 ± 35	64 ± 41	30 ± 17
Number of gill nets per fisherman	1	1	1	1
Number of traps per fisherman	8 ± 3	6 ± 3	5 ± 2	7 ± 3
Number of boats per site	16 ± 4	17 ± 2	13 ± 2	7 ± 2
Mean Catch per day (Kgday <sup>-1</sup> )	29.03 ± 9.66 <sup>a</sup>	21.28 ± 10.46 <sup>a</sup>	24.10 ± 11.70 <sup>a</sup>	2.07 ± 1.62 <sup>b</sup>

were treated as separate dependent variables. Data was log transformed since it was not normally distributed (Kolmogorov-Simonov test ( $p = 0.00$ ) and Skewness of 4.523). One-way ANOVA followed by Tukey's HSD post hoc test was used to test differences in daily catch among fishing gears, species CPUE, catch and fish length between sites. Using R-statistic software (*R version 3.0.2*; R Development Core Team 2008), non-metric multidimensional scaling (NMDS) was more appropriate in measuring community dissimilarities between study sites along the wetland. The relationship between study sites and water quality parameters was evaluated to ordinate the similarity between sites. Water quality parameters were further fitted to the ordination as vectors to identify the parameters that significantly differentiate the study sites. Stepwise multiple linear regressions with forward selection of variables were used to analyze the relationship between fish catch and water quality parameters.

## RESULTS

### Fish species composition and catch

Data on a total 5137 fish specimens were collected from all study sites over the sampling period. Six fish species dominated the wetland fish community. *C. gariepinus*, *C. liocephalus*, *C. alluaudi*, *P. aethiopicus*, *O. leucostictus*, *T. zillii* and several unidentified *Haplochromis* species were observed at all site along the wetland. *Synodontis afrofisheri* was observed only at highly disturbed Kapyani site close to Lake Lemwa. The number of species ranged from seven at the highly disturbed sites to nine at the less disturbed sites and the mean Shannon Wiener index of diversity was  $5.4 \pm 1.2$  per site. During the wet season months, a higher number of species was recorded than during the dry season months. For instance, the species richness index of 4.94 and 4.81 were realized in January and February, while 6.77 and 6.69 were realized in September and October respectively at less disturbed Nsango site.

Wetland fishery production was estimated to be 57 kg per ha per year. The number of fishermen ranged from 12 at the highly disturbed Nsango site to 27 at the less disturbed Budumba site (Table 2). Three fishing gear (gill nets, line hooks and basket traps) were dominantly used at all sites. Many fishermen used line hooks with a range of 13 hooks at the highly disturbed Nsango site to over

119 hooks at the less disturbed Budumba site. At the less disturbed Budumba and Mazuba sites, the fishermen had a high number of hooks to catch as much fish as possible within the intact wetland. Traps and gill nets were used minimally at all sites. During the rainy season, gillnets with 3.0 cm mesh size harvested more fish than other gears. Hooks were dominantly used during the dry season. More than 50% of the catch comes from the hooks fishery. Gill nets with 3.0 cm mesh size was the second most important, followed by the gill nets with 2.5 cm mesh size and traps (Figure 2). The number of hooks, gill nets of 2.5 cm mesh size and traps catch did not vary between season ( $p = 0.001$ ). But among sites, the number of hooks were significantly higher at the less disturbed Budumba site than at the highly disturbed Nsango site ( $p = 0.023$ ). The catch varied among the dominant fishing gears used. Significantly higher catch was realized by the use of line hooks than all other fishing gears ( $p = 0.001$ ). The line hooks' mean catch of  $11423 \pm 6936$  g/day was observed in the wet season and  $14863 \pm 9558$  g/day observed during the dry season which high compared to  $3294 \pm 3108$  and  $4860 \pm 4392$  g/day the wet and dry season gill nets' catch respectively.

There were temporal and spatial differences in the catch of individual fish species. Relatively higher catch was observed in the dry season than in the wet season and more at the less disturbed sites than at the highly disturbed sites (Figure 3). *C. gariepinus* and *P. aethiopicus* dominated the fishery by catch weight with a range of 0.45 kg per day at the highly disturbed Nsango site to 0.245 to 20.18 kg per day, respectively (Table 2). Catch at Nsango was significantly lower than that of other sites (Tukey's HSD test;  $p < 0.05$ ). Higher catch of both *C. gariepinus* and *P. aethiopicus* species was recorded during the dry months (January, February, July and August, Figure 3). Significantly higher catch of both species was recorded at the less disturbed sites (Budumba and Mazuba) than at the highly disturbed site (Nsango) at  $p = 0.05$  (Table 3). The disturbed Kapyani site had relatively high *C. gariepinus* catch almost the whole sampling period. The catch of small *C. liocephalus* and *C. alluaudi* was higher at the highly disturbed site than at the less disturbed sites



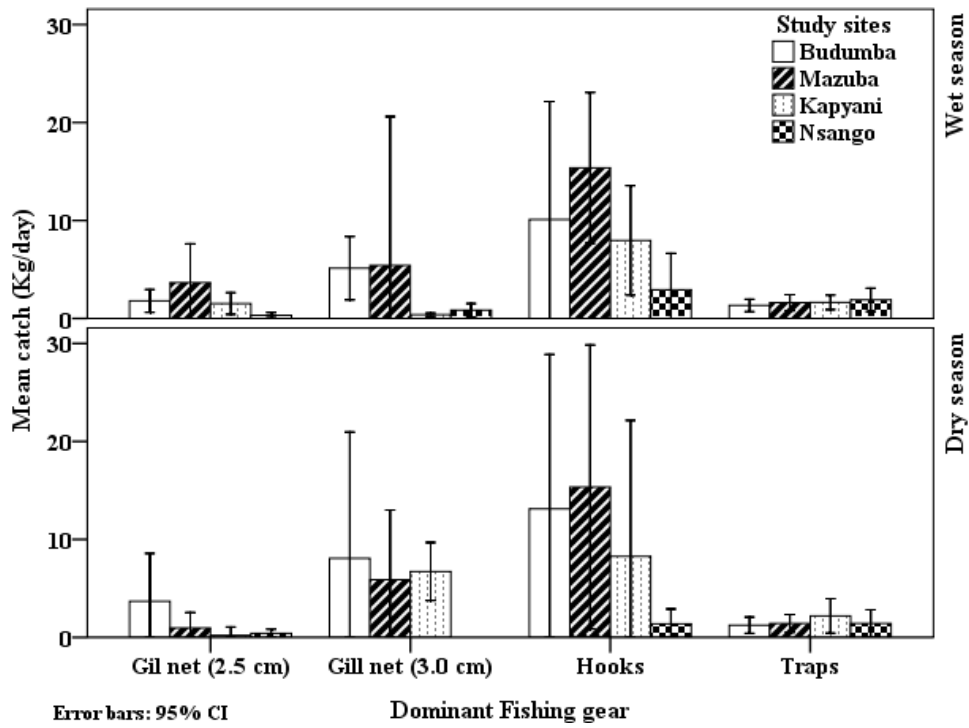


Figure 2. Seasonal mean catch of the major fishing gear at the four sites along Mpologoma wetland between September 2011 to August 2012.

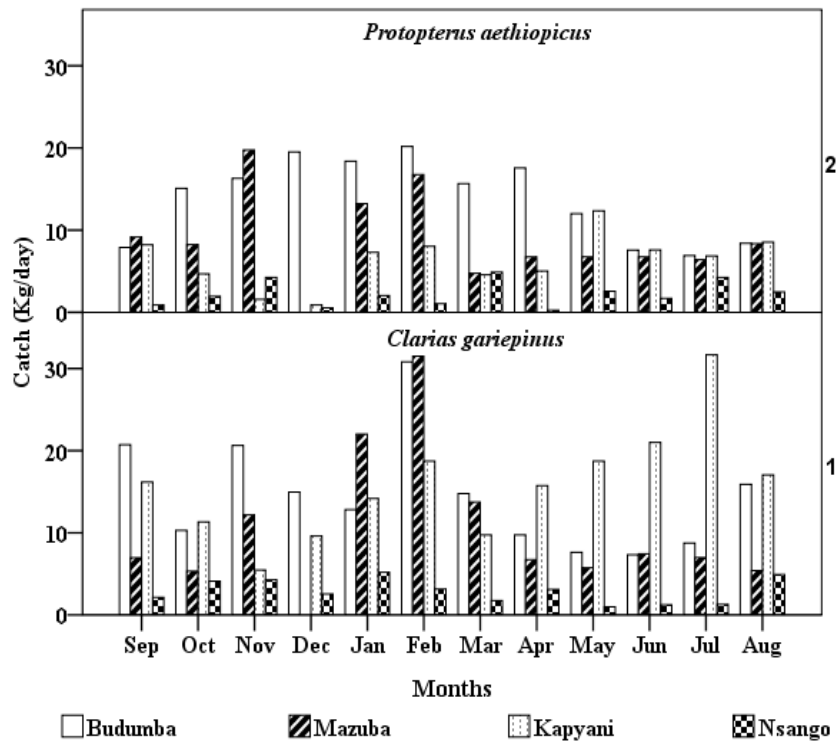
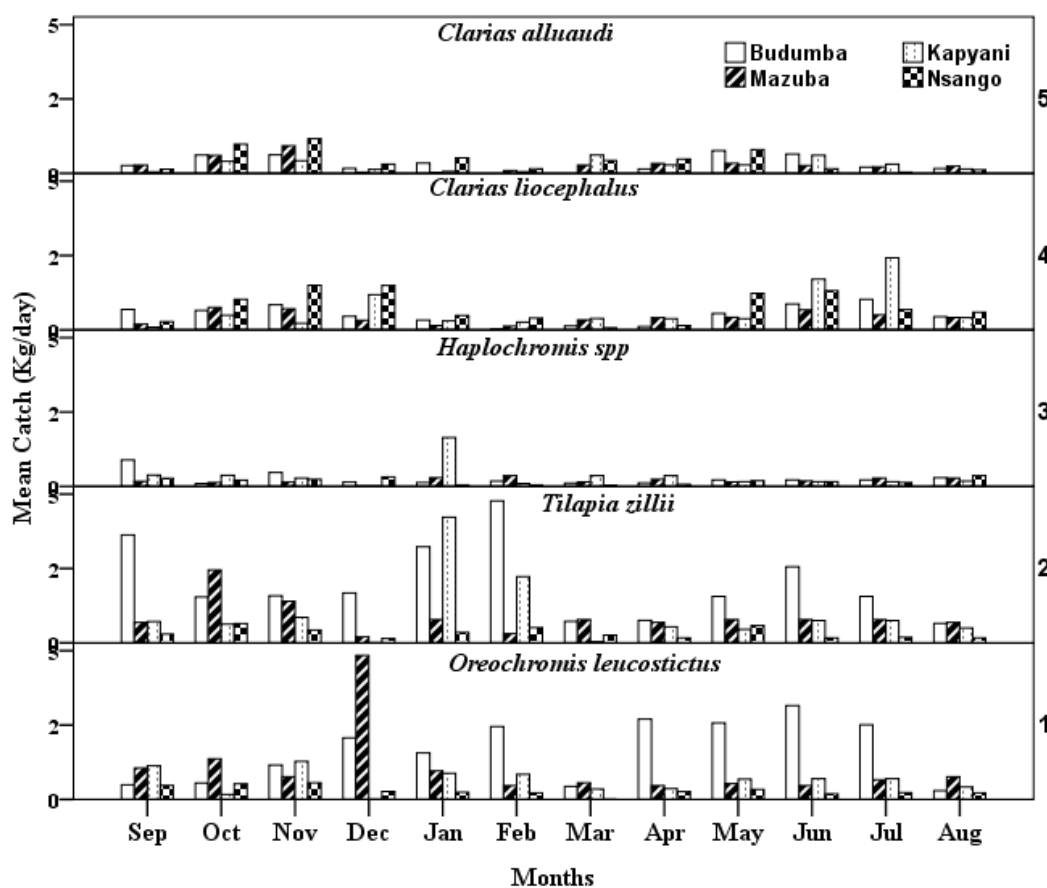


Figure 3. Mean catch of the big fish species in Mpologoma wetland fishery between September 2011 to August 2012.

**Table 3.** Mean catch (Kg/day,  $\pm$  SD) of major fish species at differently disturbed sites along Mpologoma river wetland during the sampling period.

Fish species	N	Budumba	Mazuba	Kapyani	Nsango
<i>Oreochomis leucostictus</i> Trewavas 1933	565	1.56 $\pm$ 1.07 <sup>a</sup>	1.13 $\pm$ 1.51 <sup>a</sup>	0.61 $\pm$ 0.41 <sup>a</sup>	0.29 $\pm$ 0.15
<i>Tilapia zillii</i> Garvais 1848	703	1.92 $\pm$ 1.28	0.86 $\pm$ 0.58 <sup>a</sup>	0.93 $\pm$ 1.14 <sup>a</sup>	0.32 $\pm$ 0.18
<i>Haplochromis</i> spp	1115	0.26 $\pm$ 0.25 <sup>a</sup>	0.19 $\pm$ 0.09 <sup>a</sup>	0.33 $\pm$ 0.42 <sup>a</sup>	0.19 $\pm$ 0.13 <sup>a</sup>
<i>Clarias liocephalu</i> Boulenger 1902	788	0.50 $\pm$ 0.32 <sup>a</sup>	0.42 $\pm$ 0.21 <sup>a</sup>	0.66 $\pm$ 0.70 <sup>a</sup>	0.75 $\pm$ 0.52 <sup>a</sup>
<i>Clarias alluaudi</i> Boulenger 1906	419	0.37 $\pm$ 0.24 <sup>a</sup>	0.30 $\pm$ 0.25 <sup>a</sup>	0.27 $\pm$ 0.19 <sup>a</sup>	0.42 $\pm$ 0.36 <sup>a</sup>
<i>Clarias gariepinus</i> Burchell 1815	1062	14.64 $\pm$ 6.77 <sup>a</sup>	11.28 $\pm$ 8.39 <sup>a</sup>	15.88 $\pm$ 6.56	3.05 $\pm$ 1.62
<i>Protopterus aethiopicus</i> Heckel 1851	598	13.38 $\pm$ 5.04 <sup>a</sup>	9.72 $\pm$ 4.78 <sup>a</sup>	6.47 $\pm$ 3.09 <sup>a</sup>	2.25 $\pm$ 1.46

Values in the same row with the same superscript are not significantly different ( $p < 0.05$ ).



**Figure 4.** Fish catch of the small fish species at different sites along Mpologoma river wetland between September 2011 to August 2012.

(Figure 4).

The mean CPUE for the major commercial fish species varied with fishing gear, season and study site. The CPUE for *C. gariepinus* and *Protopterus* sp was higher with the use of hooks, at the less disturbed sites than that of other fishing gear, particularly the highly disturbed Nsango

site (Table 4). At the less disturbed Budumba site, mean CPUE for *C. gariepinus* was higher (1.31 Kg100 hooks<sup>-1</sup>h<sup>-1</sup>) in the dry season as compared to 0.90 Kg 100hooks<sup>-1</sup>h<sup>-1</sup> recorded during the wet season. CPUE for the two large fish species at highly disturbed Nsango site was significantly different from that of the other sites (Tukey's

**Table 4.** Mean catch per unit effort (CPUE) for the major commercial fish species/groups at each differently disturbed site along Mpologoma wetland during both the dry and wet season between September 2011 to August 2012.

Gear type	Species	Units of CPUE	Dry season				Wet season			
			Budumba	Mazuba	Kapyani	Nsango	Budumba	Mazuba	Kapyani	Nsango
GN 2.5	<i>Haplochomis</i> spp	Kg 45 m <sup>-1</sup> h <sup>-1</sup>	0.03	0.00	0.00	0.10	0.13	0.04	0.01	0.12
	<i>C. gariepinus</i>	Kg 45 m <sup>-1</sup> h <sup>-1</sup>	0.20	0.00	0.53	0.08	0.92	0.20		
	<i>Protopterus</i> sp	Kg 45 m <sup>-1</sup> h <sup>-1</sup>	0.40	0.00			0.29			
	Small <i>Clarias</i> spp	Kg 45 m <sup>-1</sup> h <sup>-1</sup>			0.45					
	<i>Tilapia</i> spp	Kg 45 m <sup>-1</sup> h <sup>-1</sup>	0.85	0.22	0.59	0.23	0.45	0.54	0.20	0.15
GN 3.0	<i>C. gariepinus</i>	Kg 45 m <sup>-1</sup> h <sup>-1</sup>	0.35	0.40	1.60		0.46	0.49	0.20	0.36
	<i>Haplochomis</i> spp	Kg 45 m <sup>-1</sup> h <sup>-1</sup>					0.07			
	<i>Protopterus</i> sp	Kg 45 m <sup>-1</sup> h <sup>-1</sup>	0.52	0.57	0.90		0.38	0.20	0.06	
	<i>Tilapia</i> spp	Kg 45 m <sup>-1</sup> h <sup>-1</sup>	0.13	0.14			0.46	0.17		0.47
Hooks	<i>C. gariepinus</i>	Kg 100hooks <sup>-1</sup> h <sup>-1</sup>	1.31	1.10	4.50	1.20	0.90	1.85	0.76	1.20
	<i>Protopterus</i> sp	Kg 100hooks <sup>-1</sup> h <sup>-1</sup>	0.86	1.05	1.28	0.54	1.32	1.88	0.81	1.09
	Small <i>Clarias</i> spp	Kg 100hooks <sup>-1</sup> h <sup>-1</sup>	0.16	0.20	0.33	0.27	0.15	0.16	0.11	0.26
Traps	<i>Barbus</i> sp	Kg trap <sup>-1</sup> h <sup>-1</sup>	0.04	0.02		0.09		0.02		0.03
	<i>C. gariepinus</i>	Kg trap <sup>-1</sup> h <sup>-1</sup>	0.04	0.06	0.11	0.06	0.09	-	0.11	0.08
	<i>Haplochomis</i> spp	Kg trap <sup>-1</sup> h <sup>-1</sup>	0.01	0.04	0.09	0.23	0.03	0.14	0.05	0.07
	<i>Protopterus</i> sp	Kg trap <sup>-1</sup> h <sup>-1</sup>	0.05	0.12	0.12	0.05	0.06	0.12	0.12	0.07
	Small <i>Clarias</i> spp	Kg trap <sup>-1</sup> h <sup>-1</sup>	0.16	0.11	0.18	0.19	0.20	0.15	0.15	0.24

HSD test;  $p < 0.05$ ). However, the highly disturbed Kapyani site CPUE (4.50 Kg 100hooks<sup>-1</sup>h<sup>-1</sup>) was higher than the other highly disturbed Nsango site (1.20 100hooks<sup>-1</sup>h<sup>-1</sup>) in the dry season. The CPUE for *C. gariepinus* and *Protopterus* sp. showed an increasing trend during the dry months (Figure 5). While the CPUE of small fish species (*C. alluaudi*, *C. liocephalus*, *Haplochomis* spp and *Barbus* sp) did not vary significantly between season and sites ( $p = 0.05$ ).

#### Fish size

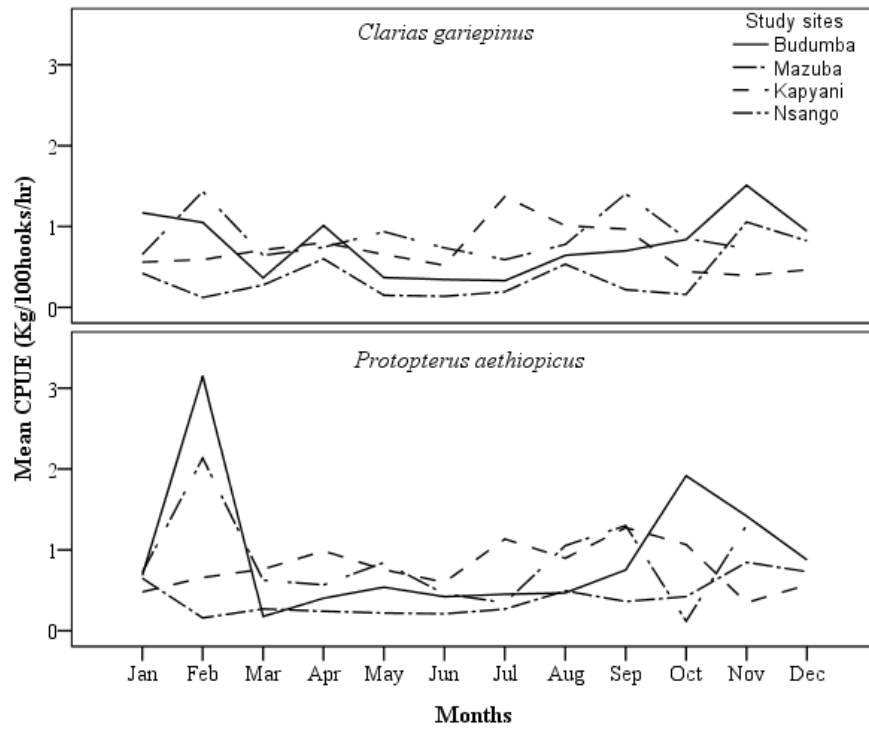
There were variations in *C. gariepinus* and *P.*

*aethiopicus* total length in the wetland with a range of 12 to 135 cm and 16 to 151 cm respectively. The mean total length of *C. gariepinus* at Budumba and Mazuba was  $47.27 \pm 20.47$  cm and  $45.32 \pm 16.76$  cm respectively. While at the highly disturbed sites (Kapyani and Nsango) the mean total length was  $41.19 \pm 21.85$  cm and  $27.33 \pm 10.98$  cm respectively. Larger fish individuals of both species were caught during the wet season (April, May and October; Figure 6). The length of these two species was significantly lower at highly disturbed Nsango site than that of the less disturbed sites ( $p < 0.01$ ; Figure 7). The less disturbed sites had larger fish even among the *Oreochomis* and *Tilapia*

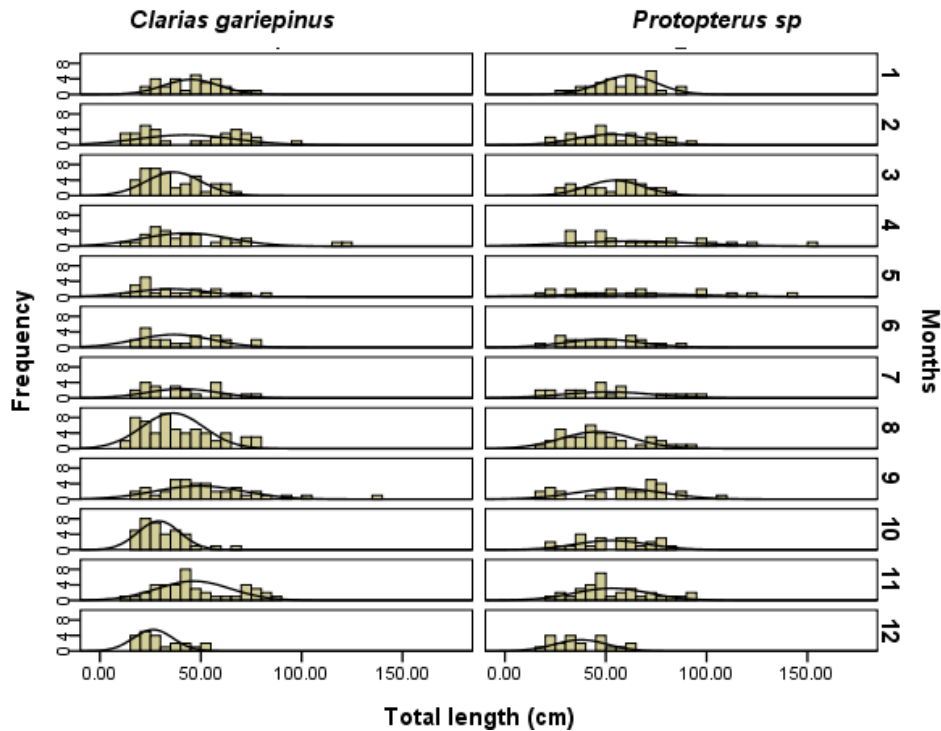
species than highly disturbed sites. However, the small fish species behaved differently. *C. liocephalus* total length ranged from 6.0 to 26.4 cm at Budumba and from 9.5 to 28.5 cm at Nsango.

#### Environmental data

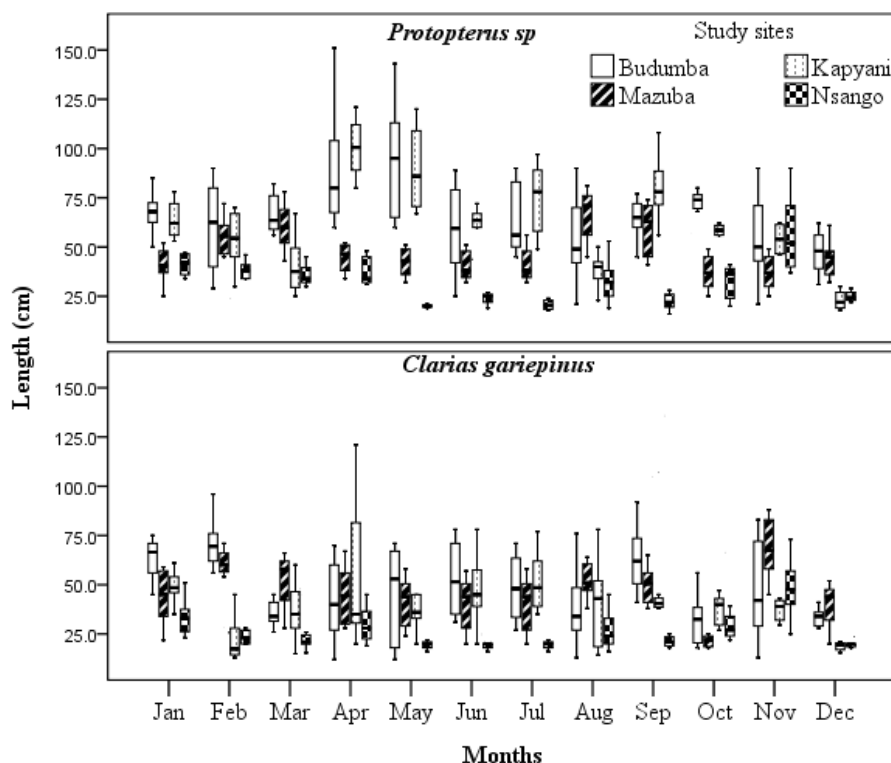
The water quality parameters varied in space and time along the wetland. Conductivity ranged from 119.9  $\mu$ S/m at less disturbed Budumba site to 406.4  $\mu$ S/m at the highly disturbed Nsango site. Conductivity at the less disturbed sites was significantly lower than that of disturbed sites and higher



**Figure 5.** Monthly mean catch per unit effort (CPUE) of the two large fish species at the four differently disturbed sites along Mpologoma wetland between September 2011 to August 2012



**Figure 6.** Length frequency distribution of two large fish species of Mpologoma river wetland fishery between September 2011 to August 2012.



**Figure 7.** Mean total length of the large fish species caught at the differently disturbed sites along Mpologoma river wetland between September 2011 and August 2012.

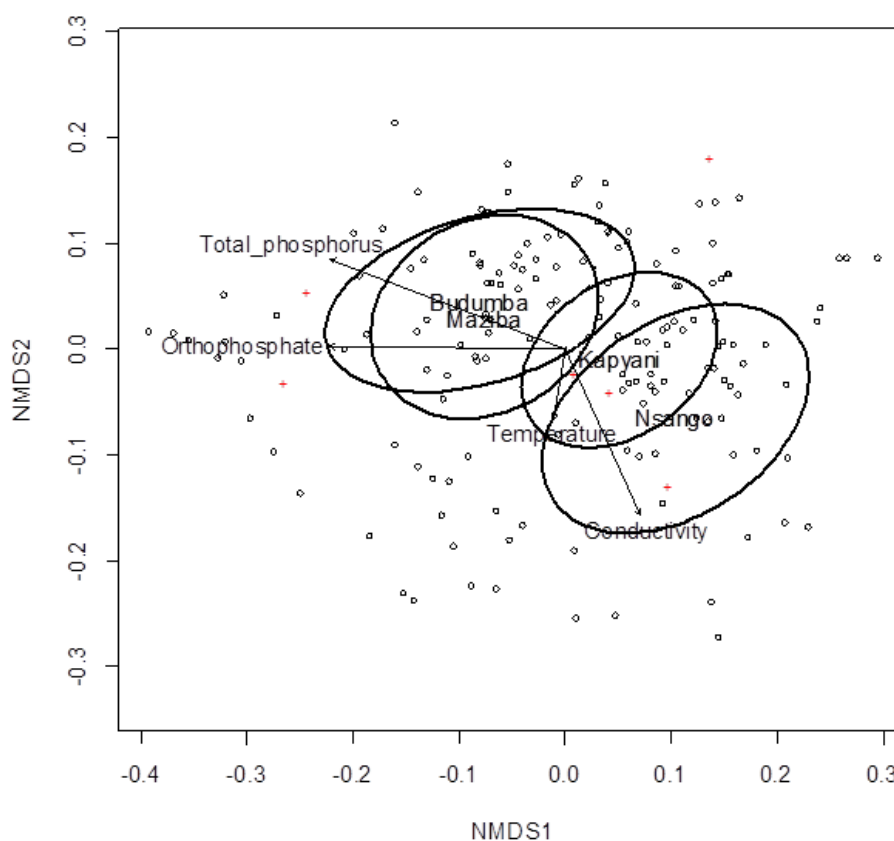
**Table 5.** Mean ( $\pm$  STD) of water quality parameters of fish habitats (inside the wetland) at the different study sites along Mpologoma River wetland (September 2011 – August 2012).

Parameter	Budumba	Mazuba	Kapyani	Nsango
DO ( $\text{mg l}^{-1}$ )	$1.35 \pm 1.03^a$	$1.98 \pm 1.26^a$	$1.58 \pm 0.67^a$	$0.96 \pm 0.76$
Temp ( $^{\circ}\text{C}$ )	$23.75 \pm 1.72$	$24.53 \pm 0.81$	$25.35 \pm 1.31$	$24.18 \pm 1.49$
Conductivity ( $\mu\text{S/m}$ )	$152 \pm 32.1^a$	$161 \pm 35.2^a$	$218 \pm 53.1^b$	$351 \pm 55.4^b$
$\text{OPO}_4^{3-}$ ( $\text{mg l}^{-1}$ )	$0.28 \pm 0.26^a$	$0.27 \pm 0.23^a$	$0.13 \pm 0.12^b$	$0.14 \pm 0.34^b$
TP ( $\text{mg l}^{-1}$ )	$0.67 \pm 0.44^a$	$0.62 \pm 0.39^a$	$0.29 \pm 0.27^b$	$0.23 \pm 0.19^b$
Water depth (m) during the dry season	$0.52 \pm 0.27$	$0.45 \pm 0.14$	$0.30 \pm 0.15$	$0.35 \pm 0.14$

Values in the same row with the same superscript are not significantly different.

during the dry months. Dissolved oxygen (DO) within the papyrus ranged between  $0.20 \text{ mg l}^{-1}$  at highly disturbed site to  $3.24 \text{ mg l}^{-1}$  at less disturbed site (Table 5). DO was high during the wet season months (April, May, October and November) with a range of 2.2 to  $4.4 \text{ mg l}^{-1}$  in the mid river. DO was low in the dry season months (January, February, June and July) with a range of 0.6 to  $1.8 \text{ mg l}^{-1}$  in the mid river section. Nitrate levels were very low to undetectable levels at all sites during the wet season while in the dry season, it ranged from 0.01 to  $0.12 \text{ mg l}^{-1}$  at the less disturbed sites and 0.03 to  $0.18 \text{ mg l}^{-1}$  at the

disturbed sites. Orthophosphate and total phosphorus ranged from 0.041 to  $1.15 \text{ mg l}^{-1}$  and 0.093 to  $1.80 \text{ mg l}^{-1}$  respectively in the wetland. From the NMDS analysis, the resulting ordination was two dimensional with final stress of 17.7 at  $p < 0.05$ . The less disturbed Budumba and Mazuba sites were identical as the distance between their circles was close to zero, while the highly disturbed Nsango site associated with a large scale rice scheme was different from the less disturbed sites as the distance between their circles was larger than zero (Figure 8). The vector analysis showed that conductivity, orthophosphate



**Figure 8.** Non-metric multidimensional scaling plot of study sites along Mpologoma river wetland. Visually fit ellipses were drawn around sites that had similar levels of water quality parameters that were significantly different between sites.

**Table 6.** Environmental vector fitting of the NMDS analysis of the water quality parameters of the different study sites.

Water quality parameters	NMDS1	NMDS2	r <sup>2</sup>	Pr(>r)
Dissolved oxygen	-0.95645	-0.29191	0.0150	0.316
Temperature	-0.15069	-0.98858	0.0651	0.07 *
Conductivity	0.41252	-0.91095	0.4269	0.001 ***
Orthophosphate	-0.99996	0.00869	0.7077	0.001 ***
Total phosphorus	-0.93377	0.35788	0.8128	0.001 ***

Significant codes: '\*\*\*', 0; 0.001 '\*\*\*'; '\*' 0.01. P values were based on 999 permutations.

and total phosphorus were significantly important in differentiating the study sites all at  $r^2$  of 0.43, 0.71 and 0.81 respectively, all at  $P < 0.001$  (Table 6).

There was a significant relationship between fish catch and water quality parameters. A strong spearman rank correlation ( $\rho = 0.501$  and  $0.348$ ;  $p < 0.05$ ) between *C. gariepinus* catch with conductivity and orthophosphate respectively was realized. *P. aethiopicus* catch was significantly correlating with conductivity, orthophosphate and total phosphorus ( $\rho = 0.510$ ,  $0.465$  and  $0.441$ ;  $p < 0.01$  respectively). With stepwise multivariate linear regres-

sion, *P. aethiopicus* catch was significantly related to conductivity and orthophosphate ( $R^2 = 0.544$ ;  $p < 0.01$ ; catch =  $-13.214 - 0.023$  conductivity +  $16.69$  orthophosphate). No significant relation was realized between water parameters and the small fish species catch and CPUE.

## DISCUSSION

The wetland is a critical refuge for a subset of Lake Kyoga fish species given the high number of similar fish

species recorded in the wetland compared to those reported in the open Lake Kyoga. *C. gariepinus*, *P. aethiopicus*, *O. leucostictus* and *Tilapia* spp. which are important Lake Kyoga fish species (NaFIRRI, 2007), were also recorded in the wetland. High diversity, similarity and endemism stem largely from the fact that nearby fresh waters were once connected by heavy floods or drainage free of barriers that enabled dispersal of fish species (Olden et al., 2010). Barriers later maintained fish species in different parts of the riverine wetland. As level of wetland disturbance increase in certain areas of the wetland, the general similarity in species was still maintained in the wetland and this was due to the fact that some fish species are considered relatively tolerant to pollution. These included *Oreochromis* species (Raburu and Masese, 2010), *P. aethiopicus*, *C. gariepinus* and *C. alluaudi* (Timmerman and Chapman, 2004). Normally reduction in species richness and abundance is expected along a degradation gradient (Raburu and Masese, 2010) and indeed at highly disturbed Nsango site, agricultural activities degraded the fish habitats that even tolerant species declined. During the relatively poor water quality periods (high conductivity and low dissolved oxygen), particularly in the dry months, at Nsango site the lowest number of fish species was recorded compared to other sites.

The Mpologoma wetland production estimate was in the order of magnitude of African floodplain production. Lightly exploited floodplain river systems produce about 40 - 60 kg ha<sup>-1</sup> yr<sup>-1</sup> of fish (Welcomme, 1985), while highly exploited tropical floodplains produce estimates more at 110 - 160 kg ha<sup>-1</sup> yr<sup>-1</sup> of fish (Bailey, 1988). The high wetland production estimated was attributed to the increased exploitation rate to cater for the increasing need to diversify livelihoods along the wetland. The complex relationship between catch (fish abundance) and effort (function of fishermen's behaviour) is what controls the catch per unit of effort (Lopes, 2011). On average, the fishermen spent almost the same time span fishing both in wet and dry season, therefore the differences in CPUE resulted from the variation in fish abundance with time at the sites. Despite the few to no full time fishermen at all sites, the fishers were able to access distant less exploited areas with abundant fish resources particularly at the less disturbed sites leading to high catch and CPUE. The fishing gears used also contributed to the variation in catch and CPUE. The record of high number of hooks per fisherman at the less disturbed sites indicated the importance of this gear to achieving high catch and CPUE. The reliability of fishing gear CPUE as an index of fish density depends on fish activity, gear selectivity, avoidance and the morphology of the fishes (Olin et al., 2010). This explained the application various fishing gear that enabled exploitation of the various fish species at the different sites, during different seasons in the wetland.

Fish species abundance is influenced by physical and chemical composition of water (Randle and Chapman, 2004), habitat size and diversity (Budy et al., 2008), and water flow patterns into the wetland (Vorwerk et al., 2009). The differences in wetland fish species abundance and catch were governed primarily by water quality parameter variation among sites, given the strong correlation between catch and conductivity at the sites. This agreed with earlier studies on floodplain fisheries which highlighted dissolved oxygen, conductivity, pH and water depth as major determinant factors to fish abundance (Louca et al., 2009). Highly disturbed sites' conductivity and dissolved oxygen levels were similar to those of highly studied polluted Nakivubo wetland in Uganda (Kansiime et al., 2007). Wetland clearing for agriculture results in dramatic alteration of the river flood curve which, leads to decrease in both the amplitude and duration of flood regime.

The wetland clearing also increases in evapotranspiration which, lead to increased salts in the water. These have pronounced impact such as high conductivity, alterations of vegetation species and cover, and decreased connectivity in wetland lagoons (Louca et al., 2009). Sustained increase in conductivity compounded by high sedimentation levels led to negative implications on the fish ecology (Chapman et al., 2003). The large rice scheme irrigation activities involve application fertilizers near Nsango site seem to have affected the water quality which, explain the reduced abundance of large fish species. Lungfish (*Protopterus* sp.) decline reflects the interaction of overexploitation and large-scale conversion of wetlands to agricultural land for the past few decades (Goudswaard et al., 2002). Such species with preferences for lower conductivities and high dissolved oxygen disappear from the wetland once these conditions persist (Goudswaard et al., 2002; Louca et al., 2009). This explains the low *C. gariepinus* and *Protopterus* species abundance at highly disturbed Nsango where those harsh conditions were observed.

Higher fish species composition abundance was recorded at the downstream disturbed Kapyani site and this was attributed to a number of factors. The interaction between the river and lake hydrology which modifies the fish habitats with modified vegetation and deeper waters (Cooper et al., 2007) allowing more fish to coexist, both wetland and open water dwelling species, despite the level of disturbance. The site was permanently connected to the nearby lakes Nakuwa and Lemwa. Also habitat recovery from disturbance during the flooding season is associated with increased food resources (Morris et al., 2007; Vorwerk et al., 2009), resulting in high fish abundance. Furthermore, wet season rice crop when cultivated as a largely rainfed crop and have little land engineering, causes less impacts on water quality and later on fish (Nguyen-Khao et al., 2005).

Temporal variation in fish species abundance and catch

in the wetland was also attributed to their reproductive traits and predator avoidance factors. Low abundance of all *Clarias* species at beginning of the rainy season along the wetland was due to their breeding cycle (Offem et al., 2010). *T. zillii* spawn at the end of the dry season (El-Sayed and Moharram, 2007) and this could explain their low abundance during the dry season in the wetland. The observed high catch at Budumba and Kapyani during the dry season was due to the high water level maintained at these two sites which, offered refuge for fish avoiding harsh conditions. *Oreochromis* sp. spawn anytime but larger quantities are observed during the rainy season (Melcher et al., 2012). Variation of small fish species abundance which breed throughout the year was attributed to avoidance of predators. High abundance of haplochromines in highly polluted areas is due to the non-avoidance of predators in turbid waters while their low abundance in less polluted areas is due to avoidance in clearer waters (Ogutu-Ohwayo, 1990).

Availability of abundant food during the rainy season is also an important factor responsible for the temporal variation in wetland fish (Offem et al., 2010). Rainy conditions lead to higher detritus, softer decomposing plant materials and low phosphorus favour in high abundance of benthic invertebrates (Hansson et al., 2005) which are important food for mainly the small fish species. Disruptions in the food base caused by alterations in water quality, particularly at highly disturbed sites, have been found to lead to higher percentage of omnivores (generalists) and a decrease in the proportions of insectivores and carnivores (Morris et al., 2007). *C. gariepinus* which is predatory (Raburu and Masese, 2010) was less abundant than *C. liocephalus*, an omnivore at highly degraded sites. Thus, feeding and reproductive strategies are among the divergent life-history characteristics that make riverine fish species respond to annual flood pulse and short-term environmental disturbances in different ways (Winemiller, 2005; Montaña et al., 2007).

The relationship between land use and small scale fishery was realized though strong relation between fish species catches and water quality parameters. The results should be of interest to resource managers because land use changes in the wetland have the potential to drastically affect the water quality, negatively impacting the production of large commercial fish species of such a small scale fishery. The wetland ecological shift phase need to be established in order for policy makers to regulate the land use change rate which may have potentially irreversible effects to both small and large fish species of this small scale fishery.

### Conflict of Interests

The author(s) have not declared any conflict of interests.

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Full Length Research Paper

## Seasonal physico-chemical and microbiological pollutants of potable groundwater in Qena governorate, Egypt: A case study

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In 9 districts of Qena governorate, Egypt, groundwater is used for human consumption. This study was carried out to evaluate the quality of these water sources. In each district, 2 wells were sampled in different seasons and physico-chemical and microbiological parameters were determined and compared with the Egyptian standards. All the tested wells had problems in physico-chemical or microbiological parameters or both. The overall seasonal magnitude of pollution was as follows: winter (45.5%) > spring (27.3%) > autumn (18.2%) > summer (9%). Permanent pollutants (pronounced in all seasons) were only physico-chemical mainly in Mn and iron. High percentages of bacterial pollutants, within wells and districts, were recorded. The highest values (for all parameters) within districts were total bacteria at 22, 35°C and total coli (88.9% for both), turbidity (66.8%), magnesium hardness, iron and manganese (66.7%), fecal streptococci (55.6%) and fecal coli (44.4%). Within the tested wells, the highest problems were total bacteria at 35 (72.2%) and at 22°C (66.7%), total coliform (61.1%) and manganese (55.6%). It is recommended to stop using these polluted sources for human consumption and to search for alternative high quality water sources or to start programs for treatment of the irreplaceable current sources.

**Key words:** Drinking water quality, physico-chemical parameters, microbiological quality, potable groundwater.

### INTRODUCTION

Groundwater is a source of potable water, in addition to treated surface water from the river Nile, in Qena governorate that is located in the South of Egypt. Nine districts belonging to Qena governorate are partially or totally depending on groundwater for drinking.

In general, groundwater is naturally replenished by

surface water from precipitation, streams and rivers (Agbaire and Oyibo, 2009). Water resources are under threat either from over exploitation or pollution caused by human activities (Efe et al., 2005). Most of the water resources are gradually becoming polluted due to the addition of foreign materials from the surroundings. These

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materials include organic matter of plant and animal origin, land surface washing, and industrial and sewage effluents (Ramachandramoorthy et al., 2010). In Egypt, the major problem is that, because population and industry are centered on the river Nile valley, all surface waters continually receive domestic sewage, agricultural drainage and industrial effluents (Sabae and Rabeh, 2007). This will affect both surface and underground water bodies on the long run (Soo et al., 2008; Hacıoglu and Dulger, 2009).

Groundwater is not as susceptible to pollution as surface water but once polluted, treatment is a long term and difficult process (Henry and Heinke, 2005; Agbaire and Oyibo, 2009). Groundwater quality is also threatened by a combination of over abstraction, chemicals such as nitrate and pesticides and microbiological contaminations from different diffusing sources (Fuest et al., 1998; Reid et al., 2003). The composition of groundwater is also affected by human activities through changes in land use and intervention in natural flow patterns (Schot and Van der Wal, 1992; Reid et al., 2003).

The World Health Organization (WHO) has repeatedly insisted that the single major factor adversely influencing the general health and life of a population in many developing countries is the access to clean drinking water (Hoko, 2005). Improved water quality normally leads to better health, increased fitness and production (Ajibade, 2004). Water quality monitoring is a helpful tool not only to evaluate the impacts of pollution sources but also to ensure an efficient management of water resources (Strobl and Robillard, 2008). Due to use of contaminated drinking water, human population suffers from a variety of water borne diseases (Manjare et al., 2010). Polluted water and inadequate sanitation kill two children every minute worldwide (Shareef et al., 2009). Diseases contracted through drinking water are responsible for 1/6<sup>th</sup> of the world's population sicknesses (WHO, 2004; Shittu et al., 2008). On the other hand, water-related diseases are responsible for 80% of all illnesses/deaths in the developing countries (UNESCO, 2007).

The quality of water is typically determined by monitoring microbial presence and physico-chemical parameters (EPA, 2003; Hacıoglu and Dulger, 2009). Pathogenic bacteria and other organisms such as viruses, protozoa and worms are the main cause of human diseases with a wide range of pathogenic microorganisms such as *Salmonella* and *Shigella* that can be transmitted to humans via water contaminated with fecal material (Kacar, 2011). Various physico-chemical parameters such as pH, alkalinity, total hardness, total dissolved solid, calcium, magnesium and nitrate have a significant role in determining the potability of drinking water (Shaikh and Mandre, 2009). Physical parameters that give rise to customer's complaints are colour, taste, odour, temperature and turbidity (WHO, 1997; Hoko, 2005).

Continuous monitoring of water quality is very essential to determine the state of pollution. This information is

important for the general public and the government in order to develop policies for the conservation of fresh water resources (Ali et al., 2000; WHO, 1997). On the other hand, groundwater exploitation schemes in the developing countries are designed without careful attention on water quality (Foster, 1995; Hoko, 2005).

Therefore, the current study was conducted to evaluate the seasonal variations in quality of the tested potable groundwater, in different districts of Qena governorate, and to what extent these waters are chemically and microbiologically contaminated.

## METHODOLOGY

Water samples were collected from 18 wells in 9 districts (two wells in each district). Samples were collected during the year 2010 in all seasons (winter, spring, summer and autumn). Three replicate samples, for each location, were collected in the morning between 9 am and 12 pm. Samples subjected to physico-chemical analysis were collected in pre-washed high density polyethylene bottles. These bottles were washed with diluted hydrochloric acid and rinsed 3-4 times with sample water. Concentrated nitric acid (3 ml) was added to the bottles subjected to iron and manganese analysis (APHA, 2005). Samples used for microbiological analysis were collected in sterilized 1 L glass bottles under aseptic conditions, kept in an ice box and transferred to the laboratory within 3 h of collection for analysis. Water pH and conductivity were recorded at the time of sample collection. All physico-chemical parameters and microbiological indicators were determined according to APHA (2005). Measurements were carried out in triplicate for all parameters and indicators. All parameters were compared with the limits of the Egyptian Ministry of Health standards (decision of the Minister of Health no. 458, 2007).

### Determination of physico-chemical parameters

The pH was determined by using "HACH Sension 156, Loveland Co., USA" pH meter. Turbidity was determined using "HACH 2100 N, USA" Nephelometer. Total dissolved solids (TDS) were determined by filtration of 100 ml sample on a 45 µm glass fiber filter connected to vacuum pump and weighing the filtrate. Electrical conductivity at 25°C was determined by using a "HACH Sension 156, Loveland Co., USA" conductivity meter. Total hardness and calcium hardness were measured by EDTA titrimetric method using Eriochrome black T and murexide as indicators, respectively. Magnesium hardness was calculated by subtracting the value of calcium hardness from the total hardness multiplied by 0.243 (APHA, 2005). Nitrate concentration was determined by measuring at 420 nm using "HACH TUV, USA" spectrophotometer and potassium nitrate for preparing the standard curve.

Iron and manganese concentrations were determined using atomic adsorption spectroscopy (Varian AA240Z, Australia). A calibration curve was prepared by using at least three concentrations of standard metal solutions. Samples were prepared by digestion with 3 ml concentrated HNO<sub>3</sub>. Then blank reagent (acidified deionized water) was introduced in the instrument followed by the sample.

### Microbiological analysis

Samples were analyzed directly after collection to minimize changes in the bacterial population. All media and chemicals were

supplied by Merck Co., England, prepared with deionized water and autoclaved at 121°C for 15 min prior to use.

#### Heterotrophic plate (total bacterial) count at 35 and 22°C

The media used were nutrient agar and buffer peptone water (APHA, 2005). The used sample volumes were 1 and 0.1 ml. Sterile agar medium was melted and kept in a water bath at 44- 46°C until used. One set of three plates was set up for each temperature. The melted medium was mixed thoroughly with sample in the plates by swirling. After being solidified, the plates were incubated for  $48 \pm 3$  h at  $35 \pm 0.5^\circ\text{C}$  and  $68 \pm 4$  h at  $22 \pm 0.5^\circ\text{C}$ . At the end of incubation, the number of colonies developed on each plate was counted to determine the plate count as colony forming unit (CFU) per ml of sample.

#### Determination of total coli, fecal coliform and fecal streptococci by membrane filter technique

The used culture media were M- Endo agar, M- FC agar, M- Enterococcus agar, Buffer peptone water, Lauryl tryptose broth, Brilliant green bile broth, Aesculin bile azide agar and EC broth as indicated for each test (APHA, 2005).

For the detection of total coliform, sample bottle was shaken vigorously and the sample filtered through 45  $\mu\text{m}$  membrane filter. The filter was then placed on the M- Endo agar plate and incubated for 22 to 24 h at  $35 \pm 0.5^\circ\text{C}$ . After incubation, red colonies with metallic golden sheen were counted as coliform bacteria. Verification of all typical and non-typical coliform colonies was carried out by picking up two typical and two atypical colonies from a membrane filter with a sterile loop, placing in lauryl tryptose broth tubes that were incubated at  $35 \pm 0.5^\circ\text{C}$  for 48 h. Tubes that produced gas were verified in brilliant green lactose broth (incubated at  $35 \pm 0.5^\circ\text{C}$  for 48 h). Gas formation in lauryl tryptose broth and confirmed in brilliant green lactose broth within 48 h were verified as coliform cultures.

#### Detection of fecal coliform

Detection of fecal coliform was carried out by repeating the steps used for total coliform on M- FC medium. The plates were then incubated for  $24 \pm 2$  h at  $44.5 \pm 0.2^\circ\text{C}$ . After incubation, colonies with blue colour were counted as fecal coliform bacteria. Verification of typical and atypical fecal coliform colonies was carried out as above in lauryl tryptose broth and gas production was verified in EC broth (tubes incubated at  $44.5 \pm 0.2^\circ\text{C}$  for 48 h). Gas formed in lauryl tryptose broth and confirmed in EC within 48 h verified the colony as fecal coliform bacteria.

#### Detection of fecal streptococci

Detection of fecal streptococci was carried out by repeating the steps used in total coliform on M- *Enterococcus* agar and the plates were incubated for 48 h at  $35 \pm 0.5^\circ\text{C}$ . After incubation, colonies with red colour were counted as fecal *Streptococcus* bacteria. All colonies that showed red, maroon or pink colour were identified as typical colonies that were verified as follows: after sample filtration, the filtrate was transferred onto a plate of bile aesculin azid agar. The plates were incubated at  $44^\circ\text{C} \pm 0.2$  for 2 h. Colonies that showed a tan to black colour in the surrounding media were counted as fecal streptococci.

## RESULTS AND DISCUSSION

The physico-chemical and microbiological water quality parameters that exceeded the Egyptian Standard Limits, are shown in Tables 1 to 9 for all the tested wells. All the other values, that were within the acceptable limits, were shown as "A" in the tables for simplicity. Parameters that exceeded the limits were as follows:

1. Abou-Tesht district: high turbidity only in El- Maharza well in winter, iron and manganese in all seasons, total bacterial counts in winter at both 22 and 35°C for the same well, in autumn (at 35°C) and autumn and summer at 22°C in El-Karnak well. Total coli was also high in winter and manganese in all seasons except summer in El- Karnak well (Table 1).
2. Farshot district: in El- Dahasa well turbidity was high in winter, Mg hardness in spring, iron and manganese in all seasons, total count at 35°C in winter and summer, total coli in winter, spring and autumn, fecal coli and fecal streptococci in spring. In El-Araky well, high Mn was recorded in autumn, TC (total bacterial count) at 35 and 22°C in summer and autumn in addition to spring at 22°C and total coli, fecal coli and fecal streptococci in spring (Table 2).
3. Nag-Hammadi district: For El-Salamya well, high turbidity and Mn were recorded in all seasons, Mg hardness in autumn, and iron and TC (at both 35 and 22°C) in winter (Table 3).
4. El- Wakf district: In Hager El- Gabal well only TC was high at both 35 and 22°C in winter and autumn. In El-Marashda well, high turbidity was recorded in winter, Mn in summer and autumn, iron in all seasons, TC at both temperatures in winter and spring and total coli in autumn (Table 4).
5. Deshna district: in El-Samata Bahary well, high turbidity was recorded in winter, Mg hardness in autumn, iron and Mn in all seasons and TC, at both temperatures, in winter and spring. In Nag- Azooz well, high values were turbidity in winter and autumn, Mg hardness in winter, total coli in all seasons except winter and both fecal coli and streptococci in autumn (Table 5).
6. Qena district: in Karm Omran well, only TC at both 35 and 22°C was high in winter and spring, at both temperatures and summer for the latter one. In Awlad Soroor well, high values were turbidity, Mg hardness and iron in all seasons except spring, total hardness in summer and autumn, Ca hardness in all seasons except winter, iron in winter and autumn, TC at 35°C in spring and autumn, TC at 22°C in spring, summer and autumn, total coli in spring and fecal streptococci in summer (Table 6).
7. Qeft district: in El- Koom El- Kebly well, high values were Mg hardness in summer and total coli, fecal coli and streptococci in autumn. In Anbar well, high values were Mg hardness in winter, spring and summer, TC at 35°C in winter and spring, TC at 22°C in the same

**Table 1.** Potable groundwater parameters above the standard Egyptian limits in Abou-Tesht district.

Wells and seasons Water quality parameters*	EI- Maharza				EI- Karnak			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Turbidity (< 1 NTU)	2.5 ± 0.0	A	A	A	A	A	A	A
Iron (< 0.3 mg l <sup>-1</sup> )	0.45 ± 0.05	0.39 ± 0.002	0.38 ± 0.004	0.45 ± 0.0	A	A	A	A
Mn (< 0.4 mg l <sup>-1</sup> )	0.59 ± 0.008	0.7 ± 0.003	0.71 ± 0.002	0.66 ± 0.014	0.53 ± 0.029	0.42 ± 0.001	A	0.55 ± 0.002
Total bacterial count at 35°C (< 50 cell/ cm <sup>3</sup> )	86 ± 4.32	A	A	A	A	A	A	89 ± 3.74
Total bacterial count at 22°C (< 50 cell/ cm <sup>3</sup> )	89 ± 0.82	A	A	A	A	A	56 ± 2.45	300 ± 0.0
Total coli (< 2 cell/ 100 ml)	A	A	A	A	5 ± 2.16	A	A	A

\*Numbers between parenthesis are the Egyptian Standard Limits according to the Minister of Health decision no. 458 (2007). A = Values are within limits, all values ± SD (n= 3).

**Table 2.** Potable groundwater parameters above the standard Egyptian Limits in Farshot district.

Wells and seasons Water quality parameters*	EI- Dahasa				EI- Araky**		
	Winter	Spring	Summer	Autumn	Spring	Summer	Autumn
Turbidity (< 1 NTU)	1.28 ± 0.0	A	A	A	A	A	A
Mg hardness (< 150mg l <sup>-1</sup> )	A	286 ± 0.82	A	A	A	A	A
Iron (< 0.3 mg l <sup>-1</sup> )	0.42 ± 0.0	0.83 ± 0.001	0.81 ± 0.0	1.43 ± 0.0	A	A	A
Mn (< 0.4 mg l <sup>-1</sup> )	0.65 ± 0.0	0.51 ± 0.0	0.52 ± 0.0	0.7 ± 0.008	A	A	0.45 ± 0.0
Total bacterial count at 35°C (< 50 cell/ cm <sup>3</sup> )	84 ± 1.63	A	74 ± 2.16	A	A	73 ± 1.63	300 ± 0.0
Total bacterial count at 22°C (< 50 cell/ cm <sup>3</sup> )	A	A	A	A	212 ± 0.82	69 ± 7.35	300 ± 0.0
Total coli (< 2 cell/ 100 ml)	6 ± 0.82	19 ± 0.82	A	67 ± 3.27	A	200 ± 0.0	A
Fecal coli ( 0.0 cell/ 100 ml)	A	1 ± 0.82	A	A	A	14 ± 0.82	A
Fecal <i>Streptococcus</i> ( 0.0 cell/ 100 ml)	A	2 ± 0.82	A	A	A	52 ± 2.16	A

\*Numbers between parenthesis are the Egyptian standard limits according to the Minister of Health decision no. 458 (2007). \*\* All values were within limits in winter. A = Values are within limits, all values ± SD (n= 3).

**Table 3.** Potable groundwater parameters above the standard Egyptian Limits in Nag-Hammadi district.

Wells and seasons Water quality parameters*	EI- Salamyia				EI- Masalha			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Turbidity (< 1 NTU)	1.75 ± 0.008	1.1 ± 0.082	1.1 ± 0.0	1.03 ± 0.0	A	A	A	1.61 ± 0.0
Mg hardness (< 150 mg l <sup>-1</sup> )	A	A	A	203.4 ± 0.082	206.6 ± 0.082	164 ± 0.816	A	A
Iron (< 0.3 mg l <sup>-1</sup> )	0.383 ± 0.0	A	A	A	0.38 ± 0.0	0.34 ± 0.0	A	A
Mn (< 0.4 mg l <sup>-1</sup> )	1.097 ± 0.0	0.92 ± 0.0	0.86 ± 0.0	0.745 ± 0.0	0.91 ± 0.0	0.65 ± 0.0	0.561 ± 0.0	0.53 ± 0.0

**Table 3.** Contd.

Total bacterial count at 35°C (< 50 cell/ cm <sup>3</sup> )	193 ± 0.82	A	A	A	A	A	A	A
Total bacterial count at 22°C (< 50 cell/ cm <sup>3</sup> )	192 ± 2.45	A	A	A	A	A	A	A

\*Numbers between parenthesis are the Egyptian standard limits according to the Minister of Health decision no. 458 (2007). A = Values are within limits, all values ± SD (n= 3).

**Table 4.** Potable groundwater parameters above the standard Egyptian limits in El-Wakf district.

Wells and seasons Water quality parameters*	Hager El- Gabal**		El- Marashda			
	Winter	Autumn	Winter	Spring	Summer	Autumn
Turbidity (< 1 NTU)	A	A	7.26 ± 0.05	A	A	A
Iron (< 0.3 mg l <sup>-1</sup> )	A	A	0.84 ± 0.0	0.8 ± 0.008	0.79 ± 0.0	0.85 ± 0.0
Mn (< 0.4 mg l <sup>-1</sup> )	A	A	A	A	0.41 ± 0.001	0.45 ± 0.0
Total bacterial count at 35°C (< 50 cell/ cm <sup>3</sup> )	64 ± 3.27	96 ± 3.27	54 ± 4.9	300 ± 0.0	A	A
Total bacterial count at 22°C (< 50 cell/ cm <sup>3</sup> )	69 ± 7.37	60 ± 8.17	60 ± 4.9	300 ± 0.0	A	A
Total coli (< 2 cell/ 100 ml)	A	A	A	A	A	14 ± 1.63

\*Numbers between parenthesis are the Egyptian standard limits according to the Minister of Health decision no. 458 (2007). \*\* All values were within limits in both spring and summer. A = Values are within limits, all values ± SD (n= 3).

**Table 5.** Potable groundwater parameters above the standard Egyptian limits in Doshna district.

Wells and seasons Water quality parameters*	El- Samata Bahary				Nag- Azooz			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Turbidity (< 1 NTU)	1.8 ± 0.082	A	A	A	1.47 ± 0.022	A	A	1.3 ± 0.008
Mg hardness (< 150mg l <sup>-1</sup> )	A	A	A	176 ± 0.29	185.5 ± 0.163	A	A	A
Iron (< 0.3 mg l <sup>-1</sup> )	0.656 ± 0.001	0.611 ± 0.001	0.601 ± 0.001	0.51 ± 0.0	A	A	A	A
Mn (< 0.4 mg l <sup>-1</sup> )	0.52 ± 0.0	0.53 ± 0.001	0.56 ± 0.001	0.59 ± 0.0	A	A	A	A
Total bacterial count at 35°C (< 50 cell/ cm <sup>3</sup> )	110 ± 7.79	67 ± 6.48	A	A	A	A	A	A
Total bacterial count at 22°C (< 50 cell/ cm <sup>3</sup> )	110 ± 7.48	67 ± 2.16	A	A	A	A	A	A
Total coli (< 2 cell/ 100 ml)	A	A	A	A	A	21 ± 0.82	24 ± 3.74	34 ± 3.56
Fecal coli ( 0.0 cell/ 100 ml)	A	A	A	A	A	A	A	2 ± 0.0
Fecal Streptococcus ( 0.0 cell/ 100 ml)	A	A	A	A	A	A	A	1 ± 0.0

\* Numbers between parenthesis are the Egyptian Standard Limits according to the Minister of Health decision no. 458 (2007). A = Values are within limits, all values ± SD (n= 3).

seasons in addition to summer and total coli in winter (Table 7).

8. Qous district: in El-Akola well, only total coli, fecal coli and streptococci were high in spring.

In Hagaza Kebly well, high Mg hardness only was recorded in spring, summer and autumn (Table 8).

**Table 6.** Potable groundwater parameters above the standard Egyptian limits in Qena district.

Wells and seasons	Karm Omran**			Awlad Soroor			
	Winter	Spring	Summer	Winter	Spring	Summer	Autumn
<b>Water quality parameters*</b>							
Turbidity (< 1 NTU)	A	A	A	1.16 ± 0.033	A	2.7 ± 0.016	1.08 ± 0.008
Total hardness (< 500 mg/l <sup>1</sup> )	A	A	A	A	A	591.6 ± 0.216	782 ± 0.497
Ca hardness (< 350mg/l <sup>1</sup> )	A	A	A	A	448 ± 0.0	379.2 ± 0.082	501 ± 0.0
Mg hardness (< 150 mg/l <sup>1</sup> )	A	A	A	152 ± 0.0	A	212.4 ± 0.082	281 ± 0.0
Iron (< 0.3 mg/l <sup>1</sup> )	A	A	A	0.32 ± 0.0	A	A	0.43 ± 0.0
Total bacterial count at 35°C (< 50 cell/ cm <sup>3</sup> )	300 ± 0.0	182 ± 7.48	A	A	300 ± 0.0	A	300 ± 0.0
Total bacterial count at 22°C (< 50 cell/ cm <sup>3</sup> )	300 ± 0.0	149 ± 4.32	99 ± 2.94	A	300 ± 0.0	150 ± 6.98	159 ± 4.55
Total coli (< 2 cell/ 100 ml)	A	A	A	A	65 ± 3.74	A	A
Fecal <i>Streptococcus</i> (0.0 cells/ 100 ml)	A	A	A	A	A	4 ± 2.16	A

\* Numbers between parenthesis are the Egyptian standard limits according to the Minister of Health decision no. 458 (2007). \*\* All values were within limits in autumn. A= Values are within limits, all values ± SD (n= 3).

**Table 7.** Potable groundwater parameters above the standard Egyptian limits in Qeft district.

Wells and seasons	EI- Koom EI- Kebly <sup>1</sup>		Anbar <sup>2</sup>		
	Summer	Autumn	Winter	Spring	Summer
<b>Water quality parameters*</b>					
Mg hardness (< 150mg/l <sup>1</sup> )	204 ± 0.0	A	197 ± 0.0	157 ± 0.0	206.8 ± 0.082
Total bacterial count at 35°C (< 50 cell/cm <sup>3</sup> )	A	A	97 ± 2.16	53 ± 2.16	A
Total bacterial count at 22 °C (< 50 cell/cm <sup>3</sup> )	A	A	136 ± 2.16	62 ± 3.56	70 ± 2.16
Total coli (< 2 cell/ 100 ml)	A	15 ± 0.82	27 ± 2.16	A	A
Fecal coli ( 0.0 cell/ 100 ml)	A	5 ± 2.16	A	A	A
Fecal <i>Streptococcus</i> ( 0.0 cell/100 ml)	A	2 ± 0.82	A	A	A

\*Numbers between parenthesis are the Egyptian standard limits according to the Minister of Health decision no. 458 (2007). 1 = All values were within limits in winter and spring, 2 = All values were within limits in autumn. A = Values are within limits, all values ± SD (n= 3).

9. Nakada district: in Asmant 2 well, high values were Mn hardness in all seasons except summer, TC at both 35 and 22°C and total coli in all seasons except spring. In Asmant 4 well, high values were Mn hardness in all seasons except spring, TC at 35 and 22°C only in summer and total coli in summer and autumn (Table 9).

Finally, the pH values for all the tested wells were within limits except for EI-Marashda well (EI-Wakf district) and Karm Omran (Qena district) that were slightly lower than limits (5.99, 5.85, respectively). No problems were found in nitrate concentrations in all the tested samples (data not shown).

The percentage of each pollutant (those values that exceeded the Egyptian standard limits) was calculated for seasons, districts and the tested wells as presented in Table 10. There were problems of pollution in all the tested wells but with variations between wells, seasons and districts for both physico-chemical and microbiological

**Table 8.** Potable groundwater parameters above the standard Egyptian Limits in Quos district.

Wells and seasons	El- Akola <sup>1</sup> Hagaza Kebly <sup>2</sup>			
	Spring	Spring	Summer	Autumn
Water quality parameters*				
Mg hardness (< 150 mgl <sup>-1</sup> )	A	199 ± 0.49	152 ± 0.74	179 ± 0.36
Total coli (< 2 cell/100 ml)	2 ± 0.82	A	A	A
Fecal coli ( 0.0 cell/100 ml)	1 ± 0.82	A	A	A
Fecal Streptococcus ( 0.0 cell/100 ml)	1 ± 0.0	A	A	A

\*Numbers between parenthesis are the Egyptian standard limits according to the Minister of Health decision no. 458 (2007). 1 = no values exceeded limits in winter, summer and autumn, 2 = No values exceeded limits in winter. A = Values are within limits, all values ± SD (n= 3).

**Table 9.** Potable groundwater parameters above the standard Egyptian limits in Nakada district.

Wells and seasons	Asmant I				Asmant II			
	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
Water quality parameters*								
Mn (< 0.4 mgl <sup>-1</sup> )	0.46 ± 0.08	0.63 ± 0.001	A	0.536 ± 0.001	0.798 ± 0.0	0.573 ± 0.0	A	0.631 ± 0.001
Total bacterial count at 35°C (< 50 cell/ cm <sup>3</sup> )	100 ± 10.8	A	300 ± 0.0	300 ± 0.0	A	A	300 ± 0.0	A
Total bacterial count at 22°C (< 50 cell/ cm <sup>3</sup> )	129 ± 8.64	A	300 ± 0.0	300 ± 0.0	A	A	300 ± 0.0	A
Total coli (< 2 cell/100 ml)	14 ± 3.56	A	200 ± 0.0	50 ± 2.16	A	A	200 ± 0.0	80 ± 5.89

\*Numbers between parenthesis are the Egyptian standard limits according to the Minister of Health decision no. 458 (2007). A = Values are within limits, all values ± SD (n= 3).

**Table 10.** Percentages of groundwater pollutants according to its appearance in seasons, districts and wells.

Pollutants (higher than limits)	Total cases (in all seasons)*	% in different seasons				% of districts and wells	
		Winter	Spring	Summer	Autumn	Districts (Total 9*)	Wells (Total 18*)
Turbidity	14	50	7.14	14.29	28.57	66.8	44.4
Total hardness	2	0.0	0.0	50	50	11.1	5.6
Ca hardness	3	0.0	33.3	33.3	33.3	11.1	5.6
Mg hardness	16	25	25	25	25	66.7	50
Iron	21	33.33	23.8	19.05	23.82	66.7	38.9
Mn	32	25	25	18.75	31.25	66.7	55.6
Total bacterial count at 35°C	22	40.9	22.7	18.2	18.2	88.9	72.2
Total bacterial count at 22°C	26	30.8	23.07	26.9	19.23	88.9	66.7
Total coli	18	22.22	22.22	22.22	33.33	88.9	61.1
Fecal coli	5	0.0	40	20	40	44.4	27.8
Fecal streptococci	5	0.0	40	40	20	55.6	33.3

\*Considered as 100% for percentage calculation.



characteristics as shown in Table 10.

Providing adequate amounts of drinking water, with an acceptable quality, is a basic necessity that ensures sustainable long-term supply of such water and is of national and international concern (Reid et al., 2003; Rizak and Hruday, 2008). Special bodies have been found to ensure that drinking water meets high standards and the product complies with legislation and safety rules (Smeti et al., 2009). For effective maintenance of water quality through appropriate control measures, continuous monitoring of large number of quality parameters (microbial and physico-chemical) is essential (EPA, 2003).

Although turbidity has no health effect, it can interfere with disinfection, provide a medium for microbial growth and indicate the presence of microbes that may be disease-causing (Shareef et al., 2009; Shittu et al., 2008). Ideal drinking water should have a turbidity value  $<1$  NTU for aesthetic quality as well as for efficient disinfection (Chakrabarty and Sarma, 2011). The obtained results (Tables 1 to 9) showed that turbidity exceeded the limits in 6 districts (66.8 %) and 8 wells (44.4%) with 50% of the total cases recorded in winter (Table 10).

As regard to pH values, it regulates most of the biological processes and biochemical reactions (Mathur et al., 2008). The recorded pH values, for different districts and wells, were within the acceptable limit except for two districts in autumn with slightly acidic pH but close to the lower limits (5.95, 5.85). Similar results (low pH levels) were recorded in wet seasons (Shaikh and Mandre, 2009; Shittu et al., 2008).

Electric conductivity (EC) of water is a direct function of total dissolved solids, organic compounds and temperature of water (Jayalakshmi et al., 2011). Conductivity of the tested water samples were all considered accepted as there were no defined limit in the Egyptian standards.

Total dissolved solids (TDS) is an important parameter for drinking water and water with high solid content is of inferior palatability and may produce unfavorable physiological reaction in the transient consumer (Abdul Jameel, 2002; Basavaraddi et al., 2012). Groundwater TDS in all wells was within acceptable limits in all seasons but close to the highest limit (data not shown). Similar high levels of groundwater TDS was reported earlier (Rao, 2006).

Water hardness is the traditional measure of the capacity of water to react with soap and hard water requires considerably more soap to produce lather. Hardness is due to natural accumulation of salts from contact with soil and geological formation or from direct pollution by human activities (Sheikh and Mandre, 2009). Hardness of the tested groundwater recorded higher values than limits only in 11.1% of districts and 5.6% of wells with 50% in both summer and autumn indicating that this is not a permanent problem in the tested wells. Calcium in water does not impart any adverse health impact but can contribute towards hardness of water (Chakrabarty and Sarma, 2011). Calcium hardness, that

exceeded the limits, recorded the same percentages, as for total hardness, for both districts and wells with a percentage of 33.3 in spring, summer and autumn (Table 10). Magnesium hardness, in the tested groundwater, was distributed among the four seasons (25% each) and was recorded in 66.7% of districts and 50% of wells (Table 10) suggesting that it is a permanent problem in the concerned wells (Tables 1 to 9).

Water containing iron does not show deleterious effect on human health but excessive iron makes the water turbid, discoloured and imparts an astringent taste to water (Trivedi et al., 2010). In the current study, most of the high iron levels were recorded in winter (33.33%) and is represented in 66.7% of districts and 38.9% of the tested wells (Table 10). Most of these values were recorded in some wells in all, or almost all, seasons representing another permanent problem in these wells (Tables 1 to 9).

Another permanent problem is the high manganese level in the tested wells. High levels of manganese were recorded in 66.7% of districts and 55.6% of wells with the highest percentage in autumn (31.25%) as shown in Table 10. Most of these values were recorded in all seasons in wells of the northern part indicating that the problem is related to the northern districts of Qena governorate.

Heterotrophic plate count (HPC) measures a range of bacteria that are naturally present in the environment (EPA, 2003; Shittu et al., 2008). Environmental Protection Agency (EPA), USA considers HPC as a primary standard based on health considerations (Shittu et al., 2008). Groundwater is usually contaminated due to improper construction, shallowness, animal wastes, proximity to toilet facilities, sewage, natural soil- plant- bacteria contact, refuse dump sites, and various human activities around the well (Bitton, 1994; EPA, 2003; Shittu et al., 2008).

In the current study, the highest total counts at both 35 and 22°C were recorded in winter season (40.9 and 30.8%, respectively). Total bacterial count is another permanent problem in Qena exhibited in 88.9% of districts and 72.2, 66.7% of wells for both temperatures (Table 10). The distribution of these bacterial contaminants is shown in Tables 1 to 9. Values of bacterial counts that exceeded the limits, after winter, were recorded in spring, summer and autumn, respectively (Table 10).

Another microbiological indicator for water quality is the total coliform bacteria (Hacioglu and Dulger, 2009). Counts higher than limits were obtained, in the current study, in different seasons and districts with the highest percentage in autumn (Tables 1 to 10). A wet season after dry one results in high loading of coliform bacteria from soil to groundwater and subsequent high coliform densities in natural spring water originating from groundwater (Pritchard et al., 2007). High counts were represented in 88.9% of Qena districts and 61.1% of the tested wells (Table 10). The high total coliform counts are

generally indicative of poor sanitary handling and/or environmental conditions affecting the wells (Dionisio et al., 2002; Ejechi et al., 2007).

Fecal coliforms are one of the most important parameters for assessing the suitability of drinking water because of the infectious disease risk (WHO, 1997). Fecal coliform indicates contamination by mammals and bird wastes (faeces) and signify the possible presence of pathogenic bacteria and viruses responsible for waterborne diseases such as cholera, typhoid, diarrhea-related illnesses and may contain human enteric pathogens (EPA, 2003). Fecal coli was found in 5 wells within 4 districts representing 27.8 and 44.4% respectively. The high loads of fecal coli bacteria were recorded in spring and autumn (40% for both) as shown in Table 10. As indicated above, for total coli, the high load of fecal bacteria is related to seasons with mild temperatures (spring and autumn) as temperature is an important factor for its growth (An et al., 2002).

Fecal streptococci is commonly used as indicator organisms for the microbiological quality of water and wastewater (Masamba and Mazvimavi, 2008). Fecal streptococci, higher than limits, was detected in 55.6% of districts and 33.3% of the tested wells. The higher percentages were recorded in both spring and summer (40%) as shown in Table 10. These results indicate that there is a pollution caused by domestic sewage and untreated human and animal waste (Mallin et al., 2000).

## Conclusions

In general, all the tested wells had either physico-chemical or microbiological problems or both. Permanent problems (exceeding limits in all seasons) were in physico-chemical parameters as follows: iron and manganese in three districts (Abou-Tesht, Farshot and Dshna), Mn and turbidity in Nag Hammadi only and iron only in El-Wakf district (Tables 1 to 9). On the other hand, microbiological pollution is obviously more pronounced within wells and districts expressed as high percentages of all the bacterial indicators (Table 10). It is therefore, recommended to carry out both chemical and microbiological treatment for the irreplaceable contaminated wells especially for those with permanent problems, as indicated above. The alternative is to avoid these wells as potable water and a search for higher quality sources should be carried out immediately.

## Conflict of Interests

The author(s) have not declared any conflict of interests.

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*Full Length Research Paper*

## Perspective of young drivers towards the care of the road traffic injured

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The existing structure of pre-hospital trauma care in developing countries is largely deficient. The goal of this study was to determine the knowledge and attitude of young drivers towards the care of the road traffic injured. This was a descriptive cross sectional study which we carried out among undergraduates of the Ladoke Akintola University of Technology Campus, Ogbomosho, Oyo state, Nigeria using a stratified random sampling technique. Of the total 457 returned questionnaire, only 396 were sufficiently filled to warrant inclusion in the study. Of this number of respondents, 80% (317) were males. The mean age of the respondents was 23 years. While 82.2% (326) of the respondents will attempt to offer victims of road traffic crash some resuscitative measures at the scene, only 30% (119) claimed to have received some form of training in first aid care of the injured. Only 0.5% (2) of the total respondents knew the universal telephone number of 112 or 911 to call in the event of road traffic crash. Young drivers are well motivated and are more likely to confront emergency situations in road traffic crashes. Training them to function as pre-hospital care provider will add to the efficacy of pre hospital care.

**Key words:** Young driver, road traffic injured, pre-hospital care, training.

### INTRODUCTION

The nature of the initial care given to the road traffic injured patient impacts significantly on the outcome of treatment. This care should be given within the frame work of a trauma system. A trauma system encompasses trauma prevention, pre-hospital care, hospital care, rehabilitation, system administration, trauma care education and training, trauma care evaluation and quality improvement, along with the participation of society (Bigdeli et al., 2010). The goal of this system is to provide early and adequate initial care for the injured patient

within the golden hour in order to reduce the morbidity and mortality that may result from such injury. The consequences of a crash can be significantly minimized by promptly providing effective pre-hospital services (Bazzoli, 1999; Elvik et al., 2004).

The existing structure of trauma care in most developing countries is largely deficient. For instance, in most of these countries, transport of road traffic victims is usually provided by relatives, taxi drivers, truck drivers, police officers and other motorists; who are usually

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untrained and have to drive along a network of poor roads (Mock et al., 2002; Kobusingye et al., 2005). It is also a common situation in a country like Nigeria to see people gather at the scene of a road traffic crash largely to catch a glimpse of what is happening. Some do volunteer to extricate and pour water over the living victims as a means of resuscitation however; most of the individuals who eventually help in the transport of these road traffic injured victims have no knowledge or training in the initial care of the injured. Significant numbers of neurological injuries appear to be a result of the extrication process or victim transportation as a result of wrong positioning and failure to protect the spine with immobilization (Cloward, 1980; Podolsky et al., 1983).

Training drivers, especially young ones, can help improve the quality immediate post crash care (Tiska et al., 2004). This is beneficial in that fellow drivers are one of the people who, driving along the road would be the first to arrive at a crash scene. If equipped with some basic skills, they can often provide care and transportation for road traffic crash victims. This education is particularly important for young drivers because by leveraging on the credibility young people have for one another, a multiplier effect can be created whereby young drivers can pass down the skills gained to their peers (Sloane et al., 1993). The power of role modeling easily plays out in this case.

The goal of this study was to find a baseline in terms of the knowledge and attitude of young drivers towards the care of the road traffic injured and further to this, develop intervention measures to help equip these young drivers with the necessary knowledge and skill in the initial care of injured road users.

## MATERIALS AND METHODS

This was a descriptive cross-sectional study which we carried out at the Ladoko-Akintola University of Technology Campus, Ogbomosho, Oyo state, Nigeria. This is a tertiary educational institution located in Ogbomosho North local government area of Oyo State. The institution was established on the 23rd April 1990 and has 6 faculties and a college and with a student population of about 25, 000. In performing this study, we obtained ethical clearance from the ethical committee of the institution. For the purpose of this study, we listed the various faculties in the institution and the departments in each faculty. Using a stratified random sampling, we selected departments to be sampled from each of the faculties.

We recruited all young drivers in the institution who are students in the selected departments, and who gave their written consent to participate in the study. For the purpose of this study, a young driver was defined as an adult between the ages of 18 and 30 years who had ever driven a vehicle on a highway in the preceding 12 months.

We used a pre-tested structured questionnaire to collate information relating to the (1) Socio-demographic characteristics of the respondents, (2) knowledge of initial care of the injured and (3) Willingness to acquire knowledge in the care of the road traffic injured. We explained the purpose of the study to the students in the departments to be included in the study, and obtained consent for the study from them. We distributed questionnaire to students in

the chosen departments who gave their written consent to the study and students who did not consent were excluded from the study.

## Data analysis

Statistical evaluation was carried out with the use of the SPSS software package (SPSS 17.0, Chicago, Illinois) and descriptive statistics was used to analyse the bi-demographic characteristics of the respondents.

## RESULTS

Of the total 457 returned questionnaire, only 396 were sufficiently filled to warrant inclusion in the study. The male respondents were 80% (317) of the total respondents. The mean age of the respondents was 23 years with a range of 16-30 years. An assessment action to be taken at the scene of an accident revealed 4.2% (17) will stand and look, 82.2% (326) will ensure first, they are not in danger before offering help and 4.6% (18) would simply walk away and hope help comes soon. Only an average of 0.5% (2) of the respondents knew either the universal telephone number of 112 or 911 to call in the event of road traffic crash (Table 1). Fifty percent (198) of the respondents said they could administer first aid to an accident victim even though only 30% (119) said they had received some form of training in first aid care. However, when asked if they were willing to have some basic training in the care of the injured, 85% (337) of the response was in the affirmative.

## DISCUSSION

Response time is considered an important criterion in assessing the quality of care provided to trauma patients (Carr et al., 2006). The role of lay people who are present at a crash scene should be to contact the emergency services; help to put out fires; and take action to secure the crash scene (Mock et al., 2002). One way of ensuring help arrives the scene of an accident early enough is having a national emergency rescue number.

Only a very small percentage of our respondents knew this number. The implication of this is that even when these young drivers are not skilled in offering first aid to accident victims, they lack the necessary information needed to seek appropriate help. When calls are able to get to the call centers from a single code, the staff at the centers can immediately re-direct the distress call to the appropriate channel and to the nearest location to the scene of the incident, for prompt rescue action. The Nigerian Communications Commission's presently works with the 112 code for telephone users to reach all emergency service like the Fire Service Commission, Federal Road Safety Commission (FRSC) and Ambulance Services.

Most of the respondents agree that ensuring their own safety was a priority ever before attempting to rescue the

**Table 1.** Showing knowledge and attitude of young drivers at the scene of an accident.

Parameter	Action at scene of accident				Emergency rescue number known		Basic training in resuscitation	
	Stand and look	Safety first	Not sure	Walk away	Yes	No	Yes	No
Frequency	17(4.2%)	326(82%) 396(100%)	36(9%)	18(4.6%)	2(0.5%) 396(100%)	394(99.5%)	119(30%) 396(100%)	277(70%)

accident victims, and fairly good number of the respondents claim they could administer first aid care to accident victims. However, only half of those who said they could administer first aid care had had any form of training in the immediate care of a road traffic injured victim. The other half with no formal training were obviously positively disposed to helping the road traffic injured and will be good candidates for a formal training.

Eighty-five percent of our respondents indicated an interest in undergoing a training that equips them to administer basic life support. Training motivated citizens, such as young drivers, who are more likely to confront emergency situations to function as pre-hospital care providers have been noted to add to the efficacy of pre-hospital care. These drivers can help improve crash scene management as is been noted that drivers are often first on the crash scene and can often offer transportation as well for the victims (Tiska, 2004). A previous study from Nigeria showed that only 6% of injured victims were transported to hospitals in ambulances while 94% were taken in private cars and public vehicles (Adeyemi-Doro et al., 1999). This adds support to the rationale of training drivers in first aid care.

It has been noted that when pre-hospital transportation is poor or absent, deaths that could have been prevented, even by inexpensive procedures, occur (Bull World Health Organ, 2005). A study in Ghana in which a total of 335 commercial drivers were trained using a 6-h basic first aid course revealed a considerable improvement in the provision of the components of first aid in comparison to what was reported before the course (Mock, 2002). In a study by Solagberu et al. (2009) in Nigeria, 60% of the victims were transported to hospitals by both relatives and by-standers from the crash scene as against those transported by ambulances of the federal road safety commission and police.

A well structured pre-hospital trauma care is at present a challenge for most developing countries. However, training motivated citizens, such as young drivers, who are more likely to confront emergency situations to function as pre-hospital care providers would go a long way in improving the outcome of treatment of victims of road traffic crash.

### Conflict of Interests

The author(s) have not declared any conflict of interests.

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