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Research Article

Physico-chemical Characteristics and Levels of Polycyclic Aromatic Hydrocarbons in Untreated Water from Ngong River, Kenya

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Abstract

River Ngong, one of the major rivers in the Nairobi river basin receives enormous amounts of solid and liquid waste from industrial and domestic discharges. This exposes the river to high pollution. An environmental concern arises especially on its unknown levels of hazardous persistent organic pollutants in particular the polycyclic aromatic hydrocarbons (PAH). Notably, its untreated water from some sections along its course is used for domestic purposes hence poses human health risks that may be attributed to long term exposure and accumulation of PAH. United States Environmental Protection Agency (US EPA) not only identifies sixteen priority PAHs that are carcinogenic and mutagenic but alongside other world bodies including WHO, have recommendations for their allowable threshold in water. Previous studies on this river have focused on pollutants such as heavy metals, microbiological contaminants, polychlorinated biphenyls and many other persistent organic pollutants. However there is no literature on the levels of PAHs in this river hence the need for this study. Data from Nairobi cancer registry indicate that cancer cases are on the rise. This can be attributed to a number of factors ranging from nutrition, physical life style to fears of exposure to possible sources of carcinogenic compounds such as PAHs. The aim of the study was to determine levels of sixteen (16) US EPA priority PAHs in water in the Ngong River and compare the levels to the WHO/US EPA standard maximum level. Physico-chemical parameters and levels of the sixteen US EPA priority PAHs in water sampled from sections along the Ngong River are reported, the latter using GC-MS. In some sampling points, turbidity, dissolved oxygen and electrical conductivity were found to divert from the recommended thresholds and overall, the total concentrations of the PAHs ranged between 2.69 ng/L and 14.22 ng/L. Although PAH levels were found to be within acceptable levels, precaution need to be adhered to in the use of untreated water from River Ngong in fear of body accumulation of PAHs and their dangers.

Keywords: Physico-chemical parameters; Polycyclic aromatic hydrocarbons; Ngong river; Nairobi river

Introduction

Environmental degradation has become a major concern globally and in particular water pollution which ranks second to air pollution in the order of important environmental issues. Persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phenols and pesticides of different chemical, physical and toxicological properties enter water bodies as a result of human activities [1]. The PAHs have a number of sources enlisted to include emissions from automobiles, industrial and domestic sources such as combustion procedures and inadvertent runoffs among others [2-4].

The existence of over 100 PAHs in the environment is increasingly becoming a concern worldwide with world water bodies across continents documenting presence of PAHs ranging from 0.001 ng/L to magnitudes of 29325 ng/L [5-8]. Irrespective of the levels, it is worth noting that these organic compounds are resistant to degradation, bioaccumulate through the food chain and are known to be carcinogenic [9-11]. Sixteen (16) PAHs are infact considered as priority by the European Union environmental protection agency, US EPA and WHO these being naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(ghi)anthracene, benzo(ghi)perylene and pyrene [12,13]. The concern therefore is that PAHs are detrimental to human beings (can impair survival and growth by causing abnormal reproduction and development), plants and animals if their levels of toxicity exceed recommended threshold [14,15].

Ngong River is one of the major rivers in the Nairobi river basin and flows through the heart of Nairobi city which is one of the major industrial cities in Kenya. The city continues to experience exponential growth in industrialization and population which has led to environmental pollution ranging from uncollected garbage, human waste from informal settlements, industrial wastes in the form of gaseous emissions, liquid effluents, agro-chemicals, and other wastes especially petro-chemicals and metals from micro- enterprises [16,17]. Consequently, the aforementioned are a direct indication to pollution of water bodies among them the Ngong River. Notably, the untreated water from some sections along the river course way is used for domestic purposes hence poses human health risks that may be attributed to long term exposure and accumulation of PAH. It is in this regard that physico-chemical parameters such as dissolved oxygen (DO), pH, turbidity, and conductivity which also provide an indication of water pollution and the levels of the 16 US EPA priority PAHs were investigated in water from Ngong River.

Materials and Methods

Chemicals and reagents

All chemicals and reagents were of analytical grade.

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Dichloromethane (DCM) hexane, high purity nitrogen, anhydrous sodium sulphate, florisil, phosphate buffer (pH 6.8), Silica gel and aluminium oxide, were obtained from Sigma Aldrich, UK. A PAH standard mix containing the 16 priority PAHs was obtained from Dr. Ehrenstofer Augsburg, Germany.

Instruments and instrumental conditions

LabQuest vernier multi-parameter meter was used for measurement of physiochemical parameters. An Agilent 7890A Gas Chromatography and 5975C Mass Selective Detector was used for the analysis of PAHs. Column oven temperature was programmed from 35 to 280°C with initial temperature maintained for 5 min then 10°C/min to 280°C for 10.5 min and then for 29.9 min at 50°C/min to 285°C. The GC was fitted with a HP-5 MS low bleed capillary Column (30 m × 0.25 mm i.d., 0.25 µm film thickness). The carrier gas was helium.

Sampling, physiochemical measurements and pretreatment

Sampling sites Mbagathi, Marter, Donholm and Kangundo along the Ngong River were selected based on the physical appearance of the water, land use patterns and surrounding economic activities. Water samples for analysis were collected directly into clean sterilized amber colored 500 mL sample bottles which had been pre-washed with distilled water and dried. Three replicate samples were collected at the same sampling point. The bottles were sealed with aluminium foil and then put in ice-box containing wet ice and then transported to the laboratory where they were kept in the fridge at -4°C prior to PAH extraction. The physico-chemical parameters, pH, temperature, conductivity, turbidity and dissolved oxygen were measured on site.

Extraction and clean-up

Extraction was carried out by liquid-liquid extraction following the procedure outlined by Anyakora and Herbert [5]. The samples were passed through glass wool to remove any sediments and coagulants. 100 ml of water was measured using a glass measuring cylinder, transferred into a beaker. Phosphate buffer was added to the samples. This was followed by addition of 20 ml dichloromethane (DCM) in a separator funnel. The mixture was shaken for 2 minutes and allowed to separate for 5 minutes. The lower organic layer was then collected into a clean and dry 250 ml conical flask and the extraction process repeated twice each time with 20 ml dichloromethane.

Sample cleanup was done using silica gel. A chromatographic column 25 cm × 1.5 cm diameter was packed with 5 g of silica gel followed by freshly baked 5 g of anhydrous sodium sulphate. The column was conditioned using 15 ml hexane and discarded. The sample extract was transferred into the column and eluted with 100 ml hexane and 100 ml dichloromethane. The eluate was then concentrated to about 3 ml using a rotary evaporator which was further reduced to about 0.5 mL using a stream of gaseous nitrogen. The concentrated extracts were then put in vials and stored in a fridge at -4°C ready for analysis.

Identification and quantification

Identity of PAHs in the samples was confirmed by the retention time and abundance of quantification/confirmation ions and mass spectra match against the calibration standards in the authentic PAHs standards. Confirmation of identity of the analytes was done using NIST/EPA/NIH MASS SPECTRAL LIBRARY (NIST 05) and NIST MASS SPECTRAL SEARCH PROGRAM Version 2.0d. Quantification of individual PAH compounds was performed by the method of internal standardization. The quantitation was based on the ratio of the peak height of the quant ion to that of the internal standard.

Results and Discussion

Physico-chemical parameters

The result obtained from physico-chemical analysis of water samples collected from different sampling points are compared with WHO and US EPA water quality standards. Table 1 shows the mean values of the physicochemical parameters at different sampling sites along the Ngong River.

pH influences the biological activity of the water microflora. During this study pH value ranged from 6.42 ± 0.00 to 6.96 ± 0.01. Except for Donholm Bridge water sample, these values are within maximum permissible limit (6.5-8.5) prescribed by WHO. However, these pH values were consistent with those for any kind of open natural water system, which vary from 5.5 to 10.5 [18]. The observed pH value indicates that the present water samples are slightly acidic. This can be attributed to deposition of acid forming substances and high organic content which can decrease the pH because of the carbonate chemistry [19]. In most cases where the water is neither very acidic nor very alkaline, the pH is regulated by the CO_2-HCO_3 system [20].

The maximum value of dissolved oxygen was noted to be 6.27 ± 0.0 mg/L at Donholm bridge water samples while the minimum value of 2.57 ± 0.09 mg/L was at Mbagathi road bridge water. The values of DO contents of water samples were above the standard limit (5 mg/L) as recommended by WHO [12] except for Mbagathi and Marter sampling points did not meet this threshold. This might be due to decay and decomposition of organic matter [20] responsible for the depletion of oxygen. The low level of DO might be due to turbidity effect which minimized the dissolve oxygen content or due to inflow of sewage with less oxygen content into the Ngong River from informal settlements such as Kibera slums.

Turbidity values fluctuated between 68.00 ± 0.64 to 85.27 ± 0.55 NTU, the minimum being in Donholm Bridge water and maximum in water from Marter bridge. High turbidity recorded in this river could be associated with sediments resulting from soil erosion from the observable farming activities and urban runoff pollution [21]. Additionally, the variations of turbidity depend on the inflow of rain water carrying suspended particles [22].

Physicochemical Parameters (n=3)					
Sampling points	pH	Dissolved Oxygen (mg/L)	Turbidity (NTU)	Temperature (°C)	Conductivity (μScm^{-1})
Mbagathi	6.96 ± 0.01^d	2.57 ± 0.09^a	69.57 ± 0.19^d	22.73 ± 0.07^d	865.00 ± 1.53^d
Marter	6.61 ± 0.00^c	2.83 ± 0.07^b	85.27 ± 0.55^a	22.37 ± 0.03^a	425.00 ± 1.53^a
Donholm bridge	6.42 ± 0.00^a	6.27 ± 0.03^d	68.00 ± 0.64^c	22.70 ± 0.06^c	646.00 ± 1.53^b
Kangundo	6.53 ± 0.01^b	5.73 ± 0.07^c	73.77 ± 0.23^b	22.67 ± 0.15^b	677.00 ± 1.53^c

Mean values followed by the same small letter within the same column are not significantly different (One-way ANOVA, Duncan's test, α=0.05).

Table 1: Mean Values of Physicochemical Parameters of water from Ngong River.

Water temperature plays an important function in the solubility of salts and gases. Additionally, chemical, biochemical and biological characteristic of an aquatic system is greatly influenced by temperature. The temperature of Ngong river water is largely influence by local climatic conditions. Values of water temperature ranged from 22.37 ± 0.03°C to 22.73 ± 0.07°C, the minimum values was recorded in winter at the Marter bridge and maximum at Mbagathi Road. The temperature difference might be due to differences between the collection times.

The conductivity of Ngong river water ranged from 425.00 to 865.00 μS cm^{-1}. The conductivity levels were found to be within values that have been reported in some water bodies from other parts of the world. For example, Sekabira et al., [23] reported conductivity levels ranging between 208.0 and 1884.0 μs/cm determined in Nakivubo Stream water in Kampala, Uganda. On the other hand the levels were lower compared to those reported in Chemu, Korle and Kpeshie lagoons, Ghana which recorded an average high conductivity of 5.677, 40.83 and 40.50 S/m respectively [7]. According to the WHO, the limit for conductivity for drinking and portable water is 700 μScm^{-1} [24]. This threshold was met in all sampling sites for both rivers except at Mbagathi Road Bridge (865.00 ± 1.53 μScm^{-1}) and Outer Ring road bridge (749.33 ± 4.26 μScm^{-1}) sampling sites where this limit was exceeded.

Levels of polycyclic aromatic hydrocarbons

The concentration (ng/L) and distribution of PAHs in water along sites on the Ngong River are presented in Table 2. Except for benzo(a)pyrene, benzo(ghi)perylene, acenaphthylene, dibenz(a,h) anthracene and acenaphthene, which were below the detection limits of the analytical instrument, eleven (11) of the priority PAHs were detected at various points along the river. Worth noting is that chrysene and benzo(a)anthracene were detected at all the sampling sites. The concentrations of the PAHs ranged from 2.32 ng/L to 14.22 ng/L, with an overall mean concentration of 11.53 ng/L. There were significant differences ($p<0.05$) in the mean concentration of PAHs at different sampling sites for all the detected PAHs except for benzo(k) flouranthene, flourene and pyrene. Although these levels are found to be below the WHO's limit of 50 ng/L [13], they fall within ranges reported in studies across the globe although in the USA and China values as high as 29325 ng/L have been reported [5-8].

The variation in the distribution of PAHs of various ring sizes along the sampling sites can be explained one, based on the surrounding activities and two, the dilution effect as the river flows. An example is the Mbagathi site which had the highest total PAHs concentration of 14.22 ng/L, is close to the expansive Kibera slums where domestic sewage outfalls into the river, while at Marter Bridge a number of industries are located around this sampling site. Furthermore, at both sites, heavy traffic is an ordinary activity. Industrial waste water and atmospheric deposition as a result of air emission from industries in addition explains the presence of the PAHs in the sampling sites. In terms of number of rings, two and three ring PAHs concentration were the lowest in all water samples although larger ring sized PAHs were detected too. Such a wide range of PAHs at different concentrations indicates that there are potentially many different sources of PAHs in the Ngong River, possibly including combustion, atmospheric fallout, oil residues, sewage discharges, outfalls and industrial wastewater [3].

Data analysis

One-Way ANOVA at 95% was employed using SPSS version 20 for windows. Values of $p<0.05$ were considered significantly different and SNKtest at $\alpha=0.05$ indicated differences among means. Student's T-test was applied for mean comparisons between means.

Conclusion

The results show an indication of some pollution in the river. However, some values of the physico-chemical parameters were found to be within acceptable range. pH levels were within the 6.5-8.5, dissolved oxygen 5 mg/L, conductivity 700 μScm^{-1} as provided by WHO. The results indicated that Ngong River is contaminated with a number of the US EPA priority PAHs. However, these levels were however below the threshold recommended by WHO and US EPA (50 ng/L). The type of PAHs detected varied from one location to another. The commonly found PAHs compounds in the water samples were fluorene, phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene,

PAHs	No.of Rings	Study sites Mbagathi	Marter	Donholm	Kangundo	p-value (0.01)	Overall Mean
	Mean ± SE (ng/L; n=12)						
Naphthalene	2	ND	ND	0.52 ± 0.06	0.14 ± 0.00	<0.001	0.33 ± 0.06
Acenaphthylene	3	ND	ND	ND	ND	ND	ND
Acenaphthene	3	ND	ND	ND	ND	ND	ND
Fluorene	3	3.14 ± 0.51	2.62 ± 0.03	ND	ND	0.33	2.88 ± 0.25
Phenanthrene	3	1.87 ± 0.02^b	1.82 ± 0.04^b	ND	0.27 ± 0.00^a	<0.001	1.32 ± 0.18
Anthracene	3	0.68 ± 0.00	0.69 ± 0.01	ND	1.28 ± 0.00	<0.001	0.88 ± 0.07
Fluoranthene	4	1.86 ± 0.04^b	1.88 ± 0.05^b	ND	0.12 ± 0.00^a	<0.001	1.28 ± 0.20
Pyrene	4	1.66 ± 0.00	1.62 ± 0.08	ND	<LOD	0.623	1.64 ± 0.04
Benzo(a)anthracene	4	2.06 ± 0.06^c	2.43 ± 0.32^c	1.18 ± 0.04^b	0.19 ± 0.00^a	<0.001	1.47 ± 0.02
Chrysene	4	2.95 ± 0.22^c	2.48 ± 0.00^b	0.24 ± 0.01^a	0.07 ± 0.00^a	<0.001	1.43 ± 0.27
Benzo(b)fluoranthene	5	ND	ND	0.07 ± 0.00	0.06 ± 0.00	0.002	0.07 ± 0.00
Benzo(k)fluoranthene	5	ND	ND	0.08 ± 0.00	0.08 ± 0.00	0.092	0.08 ± 0.00
Benzo(a)pyrene	5	ND	ND	ND	ND	ND	ND
Dibenz(a,h)anthracene	5	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	6	ND	ND	0.08 ± 0.01	0.48 ± 0.00	<0.001	0.15 ± 0.01
Benzo(ghi)perylene	6	ND	ND	ND	ND	ND	ND
∑ PAH measured		14.22	13.53	2.32	2.69		11.53

Mean values followed by the same small letter within the same row are not significantly different (One-way ANOVA, Duncan's test, α=0.05); ND: Not detected.

Table 2: Mean ± SE Concentrations (ng/L) and Distribution of PAHs in the Ngong River Water.

naphthalene, dibenz(a,h)anthracene, dibenz(a,h)anthracene and chrysene. The predominance of low and medium molecular weight PAHs (PAHs with 2-3 rings) in water from both rivers reflects petrogenic origin, related to petroleum including crude oil and its refined products. Additionally, the presence of PAHs with 4-6 rings such as fluoranthene, pyrene, benzo(a)anthracene and chrysene indicates pyrogenic origin and combustion of fossil fuels and of recent organic material. Although PAH levels were found to be within acceptable levels, precaution need to be adhered to in the use of untreated water from River Ngong in fear of body accumulation of PAHs and their dangers.

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