

High Concentrations of Polycyclic Aromatic Hydrocarbons Found in Water and Sediments of Car Wash and Kijat Areas of Winam Gulf, Lake Victoria-Kenya

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Abstract Mean concentrations of selected USEPA priority polycyclic aromatic hydrocarbons (PAHs) in surface sediments and water samples from Car Wash and Kijat areas of Winam Gulf, Lake Victoria in Kenya have been determined using GC-FID and GC-MS. Sampling was done during the rainy season in April 2006. The PAH concentrations in sediment and water ranged from 0.04 to 31.95 µg/g dry weight and 3.32 to 55.8 µg/L, respectively, depending upon the sampling location. The total concentration levels of PAHs in both the sediment and water phase in this study were found to be much higher compared with those reported from other regions worldwide, revealing significant PAH pollution of Car Wash and Kijat areas of Kisumu city bay as a consequent of anthropogenic activities as described in the text. The GC-detected PAHs were confirmed by GC-MS.

Keywords PAHs · Sediment · Kijat · Car Wash · Lake Victoria

Polycyclic aromatic hydrocarbons (PAHs) are a typical class of persistent organic compounds derived from natural sources such as forest fires and from anthropogenic emissions and discharges emanating from various sources including domestic and industrial activities. They are distributed in the aquatic environment through riverine discharge and through subsequent dry and wet deposition from long-range atmospheric transport (McVeety and Hites 1988; Gogou et al. 1996; Wakeham 1996). PAHs are

ubiquitous in the environment and recalcitrant to biodegradation. Some 16 PAHs have been recommended as priority pollutants of environmental concern by the United States Environmental Protection Agency (USEPA) because of their carcinogenicity, mutagenicity, and toxicity (Heidelberger 1976; Hallet and Brecher 1984; McVeety and Hites 1988).

Due to their hydrophobic character, PAHs rapidly become associated with suspended particles and hence with bottom sediments once they are introduced into the aquatic environment (Readman et al. 1984; Ko and Baker 1995). Contemporary sediments are considered as a 'sink' for hydrocarbons in the aquatic environment and their importance in pollution monitoring has been emphasized by many authors (Wakeham and Farrington 1980). Sediments are a good source of samples exhibiting levels of hydrocarbons which are several orders of magnitude higher than those found in the water column. Moreover, they are relatively easy to sample and to store and can be studied at different depths (Witt 1995). Sediment retention capacity for PAHs can be related to their physico-chemical properties such as organic carbon content, grain-size distribution and retention of diagenesis (Yunker et al. 1996; Baumard et al. 1998). The origin of PAHs influences their accumulation and distribution in the sediments (Hostettler et al. 1999).

Lake Victoria is situated at 0°21'N–3°0'S, 31°39'–34°53'E astride the equator on an altitude of 1,240 m above sea level with a surface area of 68,800 km². Kisumu City is situated at 0°6'S, 34°45'E on the North tip of the Winam Gulf, which is part of the Kavirondo Gulf of the Lake Victoria. It is the third largest city in Kenya as well as the principal port of the lake on the Kenyan side. It has a population of more than 322,724 according to 1999 population census. In the recent past, Jua-Kali sector (small holder industries including manufacturing and metal

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processing and fabrication) has received a lot of attention from the government and donor countries and has rapidly expanded as an important sector contributing to industrial and economic growth and job creation for the youth in the country. By 1996, the registered Kisumu Jua-Kali association had a membership of 10,000 people, occupying about 10,000 work spaces within the town, with the major activities including repairing of diesel injectors, motor vehicle overhauling, panel beating and spraying (David and Nancy 1995). Next to major motor vehicle garages are small-scale mechanics dealing with minor vehicle mechanical problems and maintenance. These garages and small-scale mechanics together discharge an estimated total load of 182,500 L of used oil to the lake per year (David and Nancy 1995). Washing of vehicles on the pavements of streets and on the shores of the lake (often referred to as Car Wash area), which started in 1960, has also recently increased as a Jua-Kali commercial activity, discharging waste water and oil spills directly into the open Gulf water. Railway wagons and tankers transporting oil to the depots located within Kisumu city pier are cleaned on site and, in addition to this, the railway harbour, which started operating in 1901, occasionally causes localized oil spills from the fuelling points. The oil and diesel spills

discharged after servicing of the trains and ships also contribute to localized pollution around this Kisumu bay. The fuel storage tanks are washed once every 5–10 years and the effluent water dumped into drains. It has been estimated that car washing, including engine washing, spill approximately 51,200 L of oil per year for an average 200 cars handled per day (David and Nancy 1995). Significant PAH pollution is therefore expected in Kisumu city bay, especially near the Car Wash area and Kisat area (with effluent from major industries in Kisumu city) where oil handling and discharges, car washing, Jua-Kali garages and major industrial effluents are concentrated. However, no previous monitoring had been done to establish the pollution status especially with reference to toxic PAHs.

This study was undertaken to establish the presence and concentration levels of the particular USEPA priority pollutant PAHs in sediment and water of Car Wash and Kisat areas of Kisumu city bay of Winam gulf, Lake Victoria in Kenya. The PAHs considered are: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene (IARC 1983).

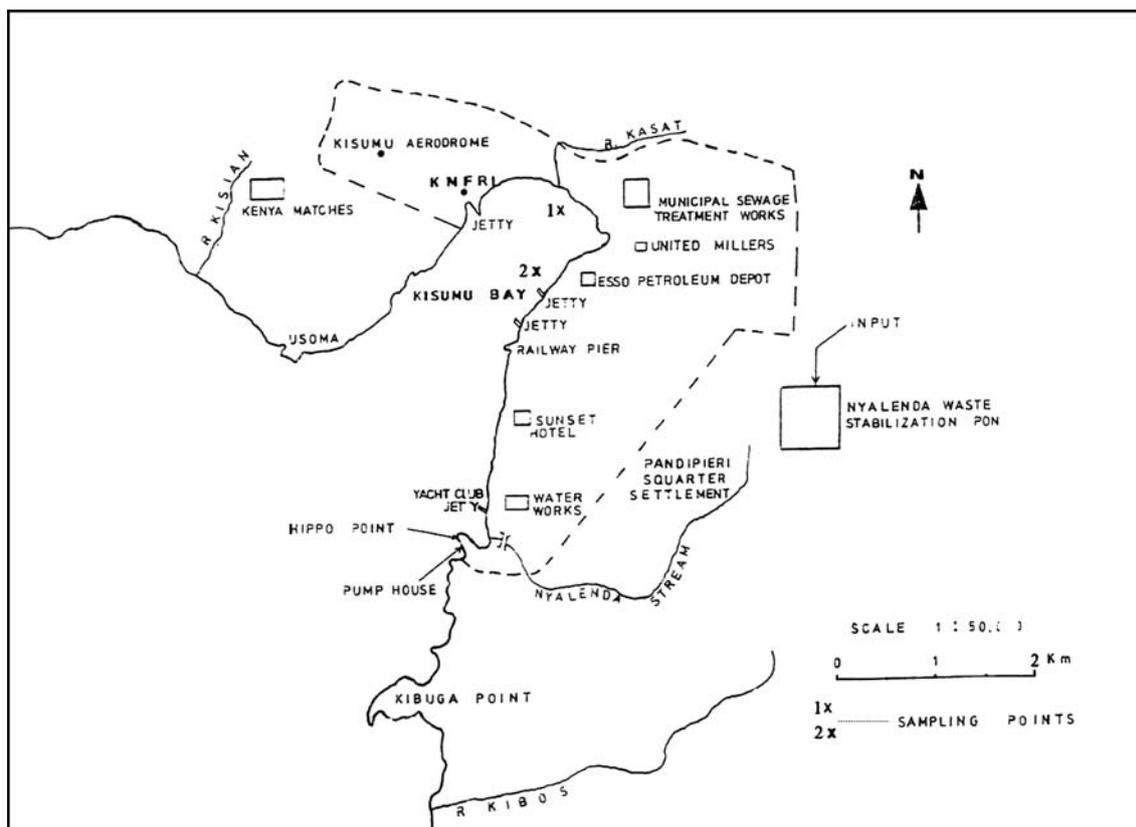


Fig. 1 Car Wash (2x) and Kisat (1x) sampling points in Kisumu City bay

Materials and Methods

Water and sediment sampling was done from the two sampling sites, Kisat (1×) and Car Wash (2×) (Fig. 1) with three replicate samples for sediment and water being taken from each of the sampling sites. Sediment samples (200 g each) were taken using a pre-cleaned sediment grab sampler at about 1 m from the shore. The samples were kept in 250-mL sample amber glass jars with lids lined with aluminium foil placed in a cooling box, with dry ice. Water sampling was done using a pre-cleaned undersurface water glass sampler about 5 m offshore and 1 m below the water surface. The water samples were kept in pre-cleaned amber 2.5 L glass bottles. The samples were then transported to the laboratory and kept at 4°C in a refrigerator while awaiting extraction.

A 50-g mass each of sediment sample was Soxhlet extracted (2 cycles/h) with 250 mL of the double distilled methanol for 4 h. After cooling for 30 min, the extract was refluxed with 25 mL of 0.7 N KOH for 2 h (UNEP 1992). The reflux mixture was then partitioned with 50 mL of *n*-hexane in a glass separatory funnel. The top *n*-hexane extract phase was dried with anhydrous Na₂SO₄ and filtered in a Buchner funnel under suction. This layer was the non-saponifiable lipid (NSL) fraction containing the non-volatile hydrocarbons (UNEP 1992). The *n*-hexane extract was concentrated to ca. 5 mL in a rotary evaporator at 40°C and then immediately kept in a deep freezer at −20°C awaiting column purification. Column purification was done using a 2 cm i.d glass column packed with 8 g of deactivated silica gel with Na₂SO₄ added to a height of 2 cm on top. The PAHs were first eluted with 15 mL hexane and then with 25 mL of 1:1 (vol:vol) hexane:dichloromethane mixture. The first 8 mL containing a large amount of aliphatic material was discarded (Christopher et al. 1995). The next eluent containing the analytes was collected and concentrated in a rotary evaporator to ca. 5 mL, and then 2 mL of toluene was added as keeper (Christopher et al. 1995). The resultant extract was further concentrated in a rotary evaporator to remove any traces of hexane and dichloromethane and the final product pipetted into a glass vial. The flask was carefully rinsed twice with 1 mL toluene and the washings added to the sample vial. The samples were kept in a deep freezer at −20°C for 4 days awaiting GC-FID analysis.

One-litre water samples were separately put in a 5-L conical flask lagged with aluminium foil to avoid light exposure and was shaken with 250 mL dichloromethane on an orbital shaker (SO1 Stuart Scientific model) for 6 h at 250 rpm (UNEP 1992). The mixture was then allowed to settle and the lower dichloromethane layer separated in a 500 mL separating funnel. The resultant emulsion layer was removed by filtering through a funnel stacked with

Table 1 PAH concentrations in water samples from Car Wash area, Winam Gulf

Nap	Ac	Ace	Fle	Phe	Ant	Flu	Pyr	BaA	Chr	B[b]F	B[k]F	B[a]P	Dib	B[ghi]	Ind
Concentrations of PAHs in water in µg/L															
47.6 ± 5.10	15.66 ± 1.10	9.12 ± 1.07	12.08 ± 0.92	9.82 ± 0.92	6.47 ± 1.15	nd	12.68 ± 0.85	6.58 ± 0.42	5.75 ± 0.47	nd	9.21 ± 0.96	15.61 ± 0.94	7.25 ± 2.10	14.61 ± 1.17	nd
Nap Naphthalene, Ac Acenaphthylene, Ace Acenaphthene, Fle Fluorene, Phe Phenanthrene, Ant Anthracene, Flu Fluoranthene, Pyr Pyrene, BaA Benzo(a)anthracene, Chr Chrysene, B[b]F Benzo(b)fluoranthene, B[k]F Benzo(k)fluoranthene, B[a]P Benzo(a)pyrene, Dib Dibenz(a,h)anthracene, B[ghi]-Benzo(g,h,i)perylene, Ind Indeno(1,2,3-c,d)pyrene, nd below detection limit															

Table 2 Showing average individual PAH accumulation ranges and weekly exposure to PAH on consumption of Car Wash water

PAH	Range ($\mu\text{g/L}$)	Weekly exposure for a 2 L consumption per day (mg)
Nap	45.26	0.63
Ac	15.66	0.22
Ace	9.12	0.13
Fle	9.39	0.13
Phe	3.39	0.05
Ant	4.37	0.06
Flu	3.53	0.05
Pyr	11.86	0.17
BaA	6.58	0.09
Chr	5.75	0.08
B[b]F	3.32	0.05
B[k]F	5.74	0.08
B[a]P	10.16	0.14
Ind	nd	nd
Dib	7.10	0.10
B[ghi]	14.19	0.20

nd below detection limit

glass wool. The dichloromethane extract layer was dried with 50 g anhydrous Na_2SO_4 with gentle swirling and filtered through a pre-cleaned glass wool in a Buchner funnel under suction. The resultant extract was concentrated in a rotary evaporator at 40°C to ca. 5 mL and then kept in a deep freezer at -20°C before column purification as described above.

The PAHs were analyzed by a GC-17A Ver. 3 SHI-MADZU using DB-17 capillary column (length, 30.0 m; internal diameter, 0.25 mm) with Flame Ionization Detector (FID). The instrument conditions were as follows: sample injection, 5 μL ; detector temperature, 310°C ; flow pressure, 77.0 kPa; total flow, 3 mL/min; column flow, 0.83 mL/min; split ratio, 2; injection mode, splitless; injector temperature, 250°C ; carrier gas, N_2 ; column sampling time, 0.5 min; column oven temperature programme, 60.0°C for 1 min, 180°C —rate 3.0 for 2 min, 250.0°C —rate 5.0 for 2 min. The GC-FID analysis was done for all

the samples, HPLC grade *n*-hexane (solvent blank), standard mix-9 and surrogate standard. In the GC-FID analysis, *n*-hexane solvent blank was first injected into the machine and its chromatogram obtained. This was followed by an injection of the external standard mix 9, then by the injection of the samples. Surrogate standard (9,10-dihydroanthracene) was then injected to help in the calculation of the recovery percentages.

The external standard mix-9 contained 10 ng/L of all the individual PAHs with different retention times. The peak area of every peak was interpreted as representing the amount of the particular PAH (from the observed R.T.) in the injected 5 μL . This was used to calculate instrument response factor for each of the PAH. The R.T. from the external standard mix-9 was then used to identify the peaks obtained for the samples and using the response factors, the ample peak areas were converted into concentrations. The percent recovery of the surrogate standard was used to correct the sample concentrations for recovery after extraction, purification and instrument analysis. The standard mix 9, one water-extract sample and one sediment-extract sample, respectively, were further analysed in a GC-MS confirm the identity of the detected PAHs. The instrument GC-MS conditions were as follows: Carrier gas, N_2 ; Capillary column, DB-5, i.d 0.25 mm; injector temperature, 280°C , splitless; Initial oven temperature, 50°C ; final temperature, 320°C ; sample injection, 5 L; programme rate, $4\text{--}6^\circ\text{C}/\text{min}$. Apart from the spectral analysis confirmation, the GC-MS retention times were found to be quite comparable with those of the GC-FID chromatograms for the standard mix 9 and the analysed sample extracts, respectively.

Results and Discussion

Concentrations of PAHs in water samples from Car Wash ranged between 3.32 and 47.6 $\mu\text{g/L}$ for 13 PAH with a mean total PAHs concentration value of 172.44 $\mu\text{g/L}$ (Table 1). Among the 13 PAHs, the concentration of naphthalene was found to be the highest (47.60 $\mu\text{g/L}$),

Table 3 Total PAH concentrations in water phase of various rivers worldwide compared with those obtained in this study

River	Year	PAH range (ng/L)	Source of data
Lower Mississippi River, USA	1999	5.6–68.9	Kwach (2008)
Elbe River, Hamburg, German	1993	107–124	Kwach (2008)
Lower Seine River, France	1993	4–36	Yunker et al. (1996)
Lower Brisben River, Australia	2002	5–12	Kwach (2008)
Gaoping River, Taiwan, China	2000	10–9,400	SEPA (2002)
Tonghui River, Beijing China	2002	193–2,651	SEPA (2002)
Middle and lower Yellow River	2004	179–369	Li et al. (2006)
Car Wash, Winam Gulf, Lake Victoria, Kenya	2006	3,320–47,600	This study

Total PAH = sum of concentrations of all the identified PAHs

possibly because of its popular domestic and industrial use in urinals in Kisumu City, in form of moth balls. The lower molecular weight PAHs e.g. Naphthalene were found to have higher mean concentrations in water samples compared to the higher molecular weight PAHs e.g. Chrysene (Table 1). Benzo(a)pyrene, a known carcinogen had a mean concentration of 15.61 µg/L which is way above the Environmental Quality Standard for Surface Water of 2.8 ng/L (GB3838-2002) (SEPA 2002).

The average accumulation ranges for individual PAHs detected in the Car Wash water samples were high indicating high weekly exposure levels of individual PAHs for aquatic life and for the human population dependent on the Car Wash water for domestic use (Table 2). Table 2 is generated using the data from our results but is based on the assumption that elimination from the body is negligible. For a person of 55 kg body weight taking 2 L of Car Wash water per day, the anthracene carcinogenic lower limit of 0.3 mg (ATSDR 1995) would be within 9 years, assuming processes of removal or excretion from the body are minimal. The lower molecular weight PAHs e.g. Nap, Ac, Ace, Fle and Phe showed higher concentrations in the water samples probably as a result of their enhanced solubilities in water although some of the higher molecular weight PAHs e.g. Pyr, B[a]P and B[ghi] also showed high concentrations in water. Solubility alone could therefore not be the concentration determining factor. The general concentration of PAHs in Car Wash water could therefore be attributed to their adsorption on suspended particulate matter (Li et al. 2006). The individual and total PAH concentrations in Car Wash water samples were very high (in the range of µg/L) compared to water phase concentrations (in the range of ng/L) reported from other regions in the world (Table 3). This indicates that Winam Gulf is highly polluted both in terms of individual and total PAHs. This high PAH pollution may be attributed to oil leaks from steamers docking at the Port of Kisumu, car washing activities in Kisumu City, oil discharge from Jua-Kali sheds and petrol stations in addition to general industrial and domestic effluent discharge carried by River Kisat into the Gulf.

The concentration of PAHs in sediment samples from Car Wash and Kisat areas ranged between 0.30 and 13.51 µg/g for 13 PAHs detected in Kisat and 12 PAHs detected in Car Wash, with mean total PAHs concentration values of 15.56 and 66.79 µg/g for Car Wash and Kisat, respectively (Table 4). The Kisat sediment samples generally showed higher mean concentrations for the individual PAH than Car Wash sediment samples (Fig. 2). Kisat sediment samples generally showed higher mean concentrations for the individual PAH than Car Wash sediment samples. This could be attributed to the sediment types from these two sampling points. The Kisat sediments, mainly from deposition by the Kisat river, were

Table 4 PAH concentrations in sediment samples from Car Wash and Kisat areas, Winam Gulf

Station	Concentrations of PAHs in sediments in µg/g (dry weight)															
	Nap	Ac	Ace	Fle	Phe	Ant	Flu	Pyr	BaA	Chr	B[b]F	B[k]F	B[a]P	Dib	B[ghi]	Ind
1×	11.77 ± 0.83	5.98 ± 0.71	4.18 ± 0.78	0.81 ± 0.01	6.98 ± 0.47	10.22 ± 0.82	0.76 ± 0.09	6.39 ± 0.32	2.81 ± 0.30	2.02 ± 1.53	nd	nd	1.36 ± 0.25	13.51 ± 0.53	nd	nd
2×	4.72 ± 0.30	nd	0.86 ± 0.07	nd	0.74 ± 0.04	1.42 ± 0.40	0.58 ± 0.03	1.10 ± 0.12	nd	0.30 ± 0.04	0.44 ± 0.02	0.38 ± 0.01	0.87 ± 0.06	nd	1.41 ± 0.22	2.74 ± 0.37

1× Kisat sampling point, 2× Car Wash sampling point, nd below detection limit

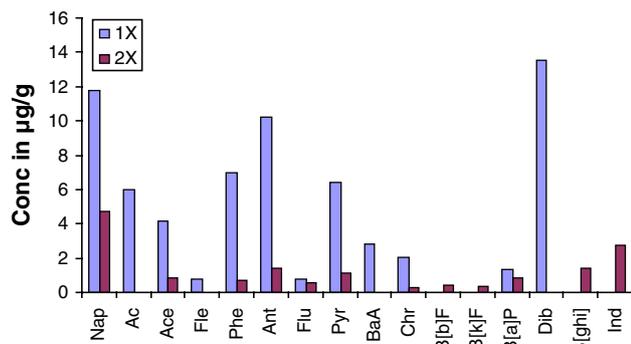


Fig. 2 Comparison of mean sediment PAH concentrations. Key: 1×—Kisat sampling point, 2×—Car Wash sampling point

coarser and silt-sized while Car Wash sediments were finer. The penetration of oil into sediments is related to the sediment type and composition. Coarser sediments allow greater penetration than fine unconsolidated sediments. Coarser sediments also have higher rates of biodegradation than fine sediments (Witt 1995). Consequently, the highest concentrations are associated generally with silt-sized sediments, which have a larger surface area (Yunker et al. 1996; Baumard et al. 1998; WHO 1998). The high concentrations of PAHs at the entrance of Kisat river into the Gulf can also indicate that pollution of the Gulf by PAH is mainly from riverine discharge from point sources rather than long range atmospheric transport and subsequent dry and wet deposition from non-point sources.

Generally, the water concentrations of individual PAHs were high in areas where their concentrations in sediments were low, whereas in cases where sediment concentrations were significantly high as shown in Fig. 3, water concentrations were lower. This indicates that sediments may be acting as a sink for PAHs in this region and are therefore important to consider when studying PAHs pollution patterns of this area.

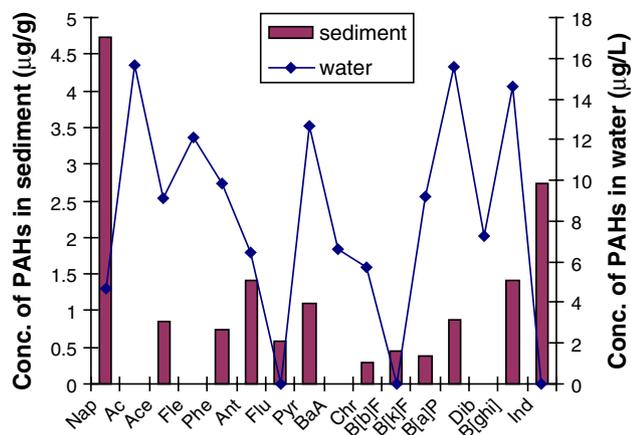


Fig. 3 Distribution of PAHs in water and sediment samples from Car Wash

In conclusion, the results obtained in this study demonstrated that pollution by PAHs in Winam Gulf was significant especially in comparison with many other rivers in the world. The concentration of B[a]P exceeded the Environmental Quality Standard for Surface Water (ATSDR 1995). The results also demonstrated that pollution of the Gulf by PAHs is mainly from effluent and riverine discharge from point sources rather than long-range atmospheric transport and subsequent dry and wet deposition from non-point sources. The relative proportions of PAHs in water and sediments are such that lower molecular PAHs accumulate more in water phase while higher molecular PAHs accumulate more in sediments in this area. The relationship study between PAHs concentrations in sediment and water samples indicated that sediments may be acting as a sink for PAHs in this Kisumu city bay area.

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