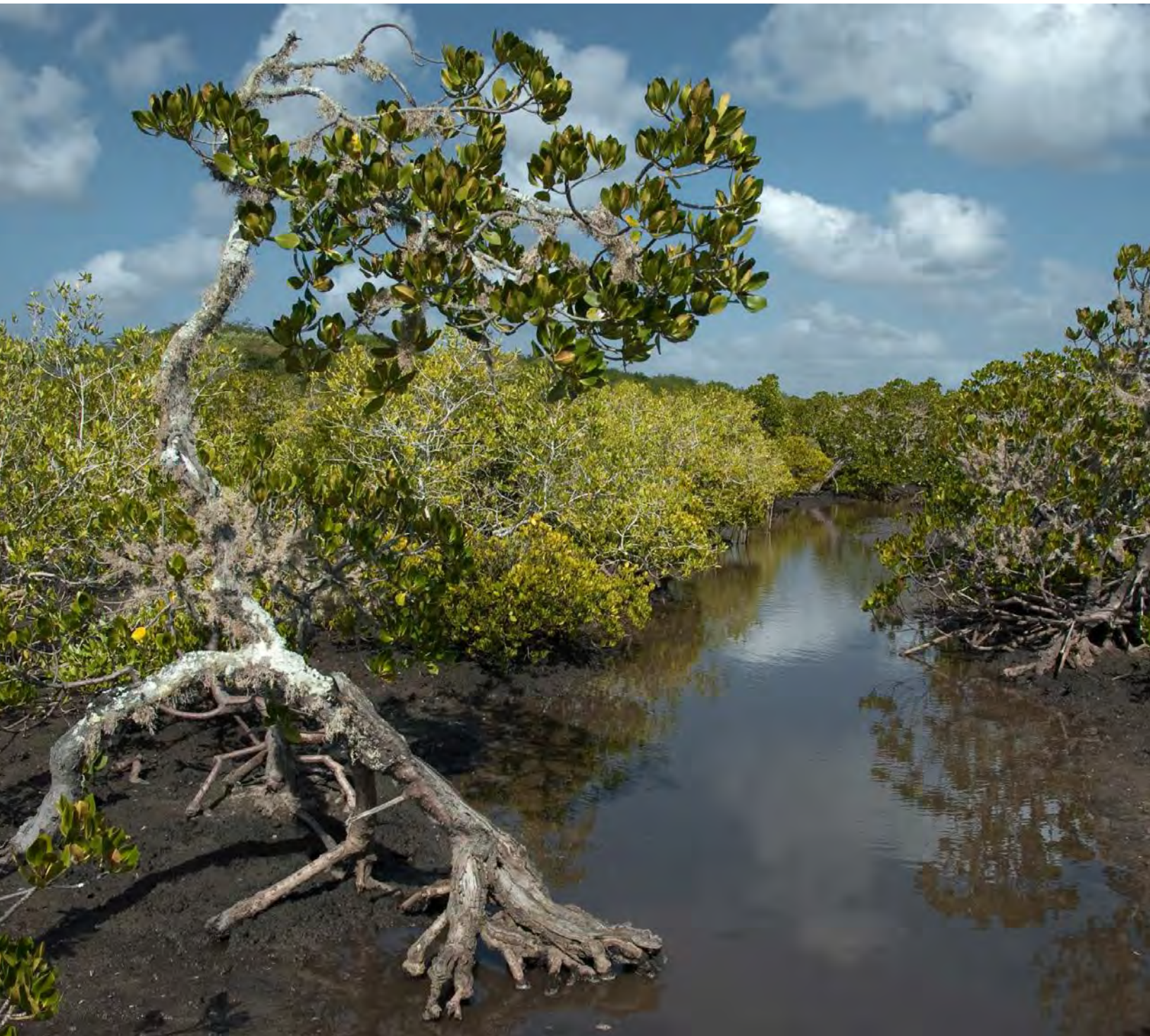
Western Indian Ocean
JOURNAL OF
Marine Science

Volume 16 | Issue 1 | Jan – Jun 2017 | ISSN: 0856-860X

Chief Editor José Paula



Western Indian Ocean
JOURNAL OF
Marine Science

Published biannually

Aims and scope: The *Western Indian Ocean Journal of Marine Science* provides an avenue for the wide dissemination of high quality research generated in the Western Indian Ocean (WIO) region, in particular on the sustainable use of coastal and marine resources. This is central to the goal of supporting and promoting sustainable coastal development in the region, as well as contributing to the global base of marine science. The journal publishes original research articles dealing with all aspects of marine science and coastal management. Topics include, but are not limited to: theoretical studies, oceanography, marine biology and ecology, fisheries, recovery and restoration processes, legal and institutional frameworks, and interactions/relationships between humans and the coastal and marine environment. In addition, *Western Indian Ocean Journal of Marine Science* features state-of-the-art review articles and short communications. The journal will, from time to time, consist of special issues on major events or important thematic issues. Submitted articles are subjected to standard peer-review prior to publication.

Manuscript submissions should be preferably made via the African Journals Online (AJOL) submission platform (http://www.ajol.info/index.php/wiojms/about/submissions). Any queries and further editorial correspondence should be sent by e-mail to the Chief Editor, wiojms@fc.ul.pt. Details concerning the preparation and submission of articles can be found in each issue and at http://www.wiomsa.org/wio-journal-of-marine-science/ and AJOL site.

Disclaimer: Statements in the Journal reflect the views of the authors, and not necessarily those of WIOMSA, the editors or publisher.

ISSN 0856-860X

Cover image: Ponta Rasa mangrove, Inhaca Island (© José Paula, 2005)

Polycyclic aromatic hydrocarbons (PAHs) contamination in coastal mangrove ecosystems of the Zanzibar archipelago

John A. Mahugija*[1], Kamaria N. Ahmed[2], Yahya M. Makame[1]

[1] Chemistry Department, University of Dar es Salaam, P.O. Box 35061, Dar es Salaam, Tanzania

[2] Ministry of Education and Vocational Training, P.O. Box 4714, Zanzibar, Tanzania

* Corresponding author: mahugija@udsm.ac.tz

Abstract

The objective of this study was to determine the levels of polycyclic aromatic hydrocarbons (PAHs) in sediments and crabs in the mangrove ecosystems of Zanzibar. Sediments and crabs from eight sampling sites were analysed for eleven selected PAHs. Samples were extracted with dichloromethane by ultrasonication, cleaned-up using column chromatography, and concentrated using a rotary evaporator. GC-MS was used in the analysis of the samples. In general, all eleven PAHs were detected in crab and sediment samples. Total concentrations of PAHs ranged from 1.70 to 28.66 ng/g fresh weight (fw) in crabs, and from 20.14 to 81.94 ng/g dry weight (dw) in the sediments. The levels of the PAHs are thought to be related mostly to petrogenic and pyrogenic sources from anthropogenic activities. The results from this study demonstrated the existence of PAHs contamination in mangrove ecosystems of Zanzibar, and it is recommended that a PAHs contamination monitoring programme be established.

Keywords: PAHs; crabs; sediments; coastal areas; Tanzania

Introduction

PAHs are among the persistent organic pollutants that are a worldwide environmental problem due to their environmental and health effects such as persistence, carcinogenicity, mutagenicity, and endocrine disrupting effects. Persistence of PAHs in the environment is related with molecular stability and hydrophobicity (Kanaly & Harayama, 2000) and the tendency of bioaccumulation through food chains resulting in adverse effects in living organisms including human beings (Eljarrat & Barcelo, 2003). Thus monitoring, control and mitigation of PAHs is an important endeavour. An increase in human activities related to sea transportation, fuel-based power generation, and the tourism industry along the coast of the Zanzibar islands, has increased PAHs emissions into the environment. The Zanzibar islands receive heavy seasonal rainfall, and the contaminants from various sources including household, vehicles, harbours and fuel stations possibly enter the coastal environment by means of waste discharges, surface runoff and aerial fallout. Monitoring of PAHs contamination in Zanzibar has not been undertaken to date, and this study provides the first information on the concentrations of PAHs in crabs and sediments from the mangrove ecosystems in the coastal areas of the Zanzibar archipelago.

Materials and Methods

Study Areas

The study was carried out in the coastal areas of the Zanzibar Islands (Unguja and Pemba). Two sampling sites were selected in Pemba, namely Ngezi and Wesha, and six in Unguja, located at Bumbwini Makoba, Jozani, Donge Muwanda, Kinazini, Mbweni, and Maruhubi. The locations of the sites are shown in Figs. 1 and 2.

Among the sampling sites, five had high levels of anthropogenic activities, while the remaining three had low levels of anthropogenic activities. Ngezi, which is in the northern part of Pemba Island, is a government protected forest site. At Wesha, there are many anthropogenic activities that are carried out including day-to-day shipping operations, diesel-run

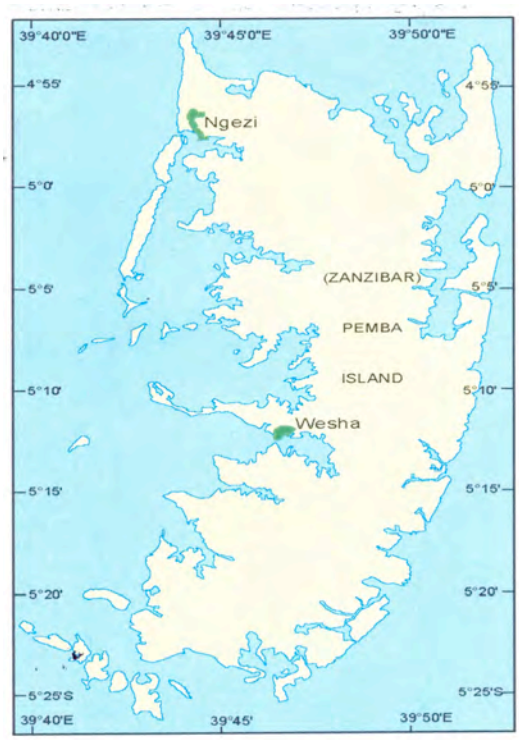


Figure 1. Map showing the location of sampling sites in Pemba Island.

electric power generation, and fuel transfer from tankers into receiving facilities which are often associated with oil spills. Other human activities include the burning of firewood and charcoal, fishing activities, boat/dhow making, and fishing machinery servicing. The coastal area of Wesha also receives contamination from road smelters.

Jozani is located in south west Unguja Island. The Jozani mangroves and wetlands are a government protected forest reserve. Within this area there are low anthropogenic activities. Donge Muwanda is in northern Unguja Island. There are extensive fish processing activities in this area, including smoking and roasting on the beach, which use a lot of firewood. Kinazini mangrove ecosystem is in an urban area of Zanzibar Island. It receives domestic waste and other anthropogenic waste products from Zanzibar town which are discharged directly into the mangrove ecosystem of Kinazini. Marine transportation, car washing, service stations, and boat/dhow making and servicing activities are also carried out in this area.

Maruhubi is in an urban area of Zanzibar Island near Kinazini. Within the coastal area of Maruhubi fuels are combusted and petroleum products are used during boat/dhow making and servicing activities. Maruhubi receives both domestic and industrial wastes. Sewage wastes from hotels and domestic wastes discharge directly into the Maruhubi coastal area. There is also a transfer point for oil from tankers into receiving facilities at the Mtoni depot near Maruhubi. The Bumbwini Makoba site is in northern Unguja Island. Anthropogenic activities including the combustion of wood fuels, boat/dhow making and repairing of fishing machinery are carried out in the vicinity of the mangrove ecosystem. The Mahonda sugar and alcohol factories are also located close to this area. Within the coastal areas of Mbweni, which lies just south of Zanzibar town, marine transportation and servicing activities occur which use petroleum-based fuels. There are also hotels and residential areas near this site.

Sample collection

Sampling of sediments and crabs was conducted in July and October 2013 at eight sites. For each site, sediment samples were taken at three different points of at least 10 meters apart, starting from near the sea (lower), middle (middle), and furthest from the sea (upper). Surface sediment samples (15 cm deep) were collected from the sampling sites using clean shovels. Crab samples were collected from the selected sampling sites using iron traps. Duplicate crab samples were collected randomly at the same sampling sites. A total of twenty-four sediment samples and twelve crab samples were collected. The samples were

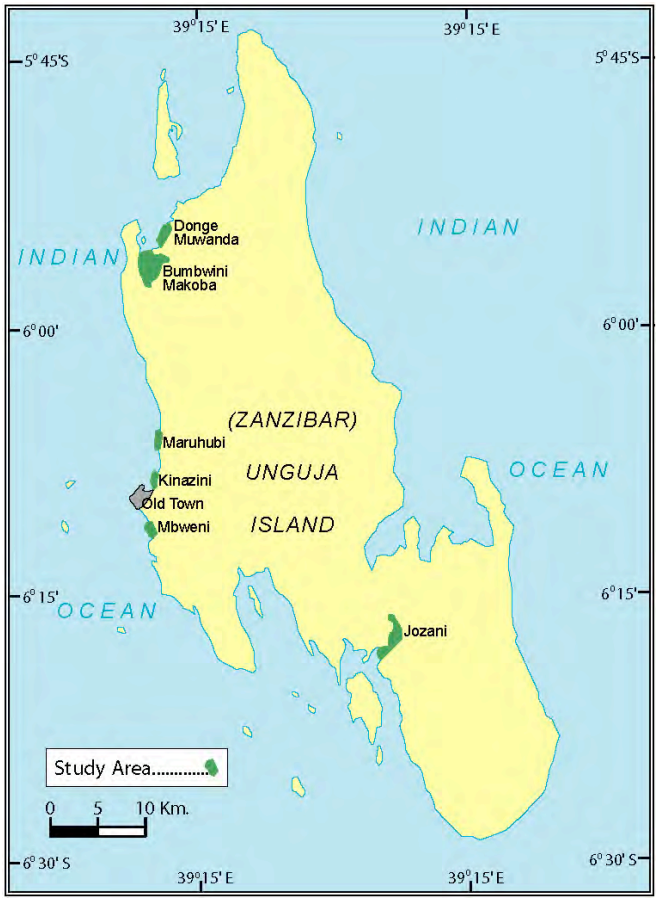


Figure 2. Map showing the location of sampling sites in Unguja Island.

wrapped separately in aluminium foil, transported to the laboratory and stored in a freezer at a temperature below -18 °C until extraction.

Extraction of PAHs

The procedures used by Nasr *et al.* (2010) were adopted for extraction of PAHs in sediments and crabs. Subsamples of sediments (20 g each) were weighed for the determination of dry weights and analysis of PAHs. Each sediment sample was homogenised with 40 g of anhydrous sodium sulphate using a mortar and pestle and added a 250-ml bottle, after which dichloromethane (60 ml) was added and shaken on an ultrasonic bath for 2 h. The extract was decanted and the extraction was repeated twice with 30 ml dichloromethane. The fractions were combined and concentrated in a rotary evaporator at 40 °C up to 2 ml. Cyclohexane (5 ml) was added and concentrated further to 2 ml. Crab soft tissues (20 g) from the body were taken for each sample for the determination of the concentrations of PAHs. Each sample was homogenised by grinding with anhydrous sodium sulphate (40 g), and extracted by shaking with dichloromethane (60 ml) in an ultrasonic bath for 2 h. The extracts were decanted and the sample was shaken again with dichloromethane (30 ml) and left for a night. The combined extracts were concentrated in a rotary evaporator at 40 °C to 1 ml. The solvent was replaced with cyclohexane and concentrated further to 2 ml.

Clean-up of Sample Extracts

Clean-up to remove interferences from extracts was carried out by adsorption column chromatography as per Nasr *et al.* (2010). The adsorbents (silica and alumina) were activated by heating at 130 °C for 12 h and then cooled at room temperature. Alumina was deactivated by adding 5% distilled water. Traces of sulphur in the extracts were removed using activated copper following the procedure described by Gaspare *et al.* (2009). To prepare the activated copper, dilute hydrochloric acid (1.0 M, 20 ml) was added into an Erlenmeyer flask containing copper crystals (20 g). The mixture was shaken for 1 h using an ultrasonicator and then decanted. The decanted activated copper was repeatedly washed with enough distilled water to remove all traces of the acid to avoid degradation of the analytes, and then rinsed with dichloromethane (50 ml) for 1 h. The column was packed with silica gel

(5 g) and alumina (3 g) and rinsed with dichloromethane (5 ml). The extract was added into the column and eluted with a mixture of dichloromethane (20 ml) and cyclohexane (30 ml). For clean-up due to the deposition of sulphur in the sediment extracts, activated copper (1 g) was added to the extract; the mixture was shaken for 10 min and decanted. The extract was concentrated using a rotary evaporator at 40 °C, the solvent replaced with cyclohexane:acetone (9:1), and 1.5 ml of extract was transferred to a vial ready for analysis.

Analysis, Identification and Quantification of PAHs

Gas chromatography-Mass spectrometry (GC-MS) analyses of the cleaned extracts were carried out at the Chemistry Department, University of Dar es Salaam using a Shimadzu GC-MS QP2010 Ultra. The GC processes included: an autosampler, injection volume of 1 µl, injector temperature of 250 °C, pressure of 150 kPa, splitless injection mode with a purge flow of 3 ml/min, helium as carrier gas with flow rate of 2.17 ml/min and average velocity of 54.6 cm/sec, capillary column (Rtx-5MS, 30 m length, 0.25 mm id, and 0.25 µm film thickness), column temperature programme of 90 °C, held for 2 min, then increased at 5 °C/min to 320 °C, held for 12 min and interface temperature of 300 °C. The mass spectrometer processes included: electron impact (EI) ionization, ion source temperature of 230 °C, detector temperature of 300 °C, and full scan mode for the masses between 45 and 500 m/z. The PAHs in the samples were identified by comparing retention times and mass spectra of the analytes against those of standards. Typical retention times and selected masses of the PAHs are shown in Table 2. Quantification of PAHs was performed under known concentrations of the external standards and using peak heights. The mass fragment with the highest intensity was used for quantification (Table 2). Eleven members among the 16 US EPA priority PAHs were analysed.

Analytical Quality Assurance

The samples were wrapped with aluminium foil and kept in clean containers. The chemicals (solvents, reagents and standards) used were of analytical grade and high purity (above 98%). The tools and glassware were cleaned using water and liquid soap followed by rinsing with distilled water and acetone and then the glassware was dried in an oven at 150 °C. Blanks, recovery tests and detection limits were determined. The detection limits were established based on a 3:1 signal to noise ratio. Mixed standards with concentrations of 1-8.33 ppb were spiked into the blank samples (crab and sediment) that were obtained from the Jozani site for recovery tests. The recovery values of PAHs from crabs and sediments (n = 6) ranged between 74.2 and 116.7%, and were deemed acceptable. The detection limits for crabs and sediments ranged from 0.002 to 0.009 ng/g for naphthalene, acenaphthylene, fluorene, anthracene, benzo[a]anthracene, and benzo[k] fluoranthene, and from 0.012 to 0.036 ng/g for benzo[a]pyrene, benzo[b]fluoranthene, indeno[1,2,3-cd] pyrene, benzo[ghi]perylene, and dibenzo[a,h]anthracene. Analytes that gave results below these limits were considered as 'not detected'.

Table 1. A List of PAHs analytes, their retention times and GC-MS masses.

PAHs	Retention time (min)	Quantification mass (m/z)	Qualifying ions (m/z)
Naphthalene	5.89	128	127 – 129
Acenaphthylene	11.77	152	76 – 151
Fluorene	14.83	166	82 – 165
Anthracene	19.06	178	76 – 176
Benzo[a]anthracene	31.14	228	226 –229
Benzo[k]fluoranthene	35.84	252	250 – 253
Benzo[a]pyrene	35.94	252	126 – 253
Benzo[b]fluoranthene	37.06	252	126 – 250
Indeno[1,2,3-cd]pyrene	41.15	276	138 – 277
Dibenzo[a,h]anthracene	41.33	278	139 – 279
Benzo[g,h,i]perylene	41.96	276	138 – 277

Data Analysis

Statistical analyses of the data were performed using Graphpad InStat (Motulsky, 1998). The One-way ANOVA and *t*-test were applied to determine the differences in the concentrations of PAHs in crab and sediment samples. Correlations in the concentrations of PAHs between crabs and sediments were checked using the Pearson's correlation test. All statistical analyses were based on the significance level of $p = 0.05$.

Results and Discussion

PAHs in Crab Samples

PAHs Detection and Concentrations in Crabs

The concentrations of the PAHs in crab samples are shown in Table 2 and the levels and detection frequencies are summarised in Table 3. PAHs were detected in most crab samples with concentrations up to 5.40 ng/g, except for indeno[1,2,3-cd]pyrene, and dibenzo[a,h] anthracene, which were detected in 33.3 and 16.7% of

Table 2. Concentrations of PAHs in crab samples (ng/g fw).

Sampling Site	Wesha		Jozani		Kinazini		Ngezi		Mbweni		Bumbwini Makoba	
PAHs/category	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**	**Range**	**Mean**
Naphthalene	ND-3.31	1.66	0.03-0.86	0.45	0.83-3.15	1.99	0.17-2.15	1.16	ND-2.33	1.17	0.62-1.99	1.31
Acenaphthylene	0.13-2.41	1.27	0.05-0.15	0.10	0.15-1.89	1.02	0.15-1.31	0.73	0.17-1.46	0.82	0.19-1.35	0.77
Fluorene	0.35-3.09	1.72	0.06-0.35	0.21	0.32-2.77	1.55	0.41-1.90	1.16	ND-0.56	0.28	0.64-1.67	1.16
Anthracene	0.37-3.12	1.75	0.30-0.55	0.43	0.61-2.96	1.79	0.64-1.73	1.19	0.68-1.98	1.33	0.96-1.74	1.35
Benzo[a]anthracene	1.48-4.32	2.90	0.45-0.60	0.53	0.83-3.42	2.13	1.70-4.56	3.13	0.86-1.96	1.41	0.27-5.40	2.84
Benzo[k]fluoranthene	0.14-2.64	1.39	0.17-0.38	0.28	0.09-1.92	1.01	0.25-1.30	0.78	0.15-1.20	0.68	0.08-1.73	0.91
Benzo[a]pyrene	0.03-2.43	1.23	0.11-0.16	0.14	0.14-1.93	1.04	0.17-1.54	0.86	0.02-1.23	0.63	0.09-1.57	0.83
Benzo[b]fluoranthene	0.47-2.91	1.69	0.20-0.31	0.26	0.30-2.30	1.30	0.53-2.80	1.67	ND-1.30	0.65	0.04-1.79	0.92
Indeno[1,2,3-cd]pyrene	ND	ND	0.33-0.48	0.41	ND-0.73	0.37	ND-1.09	0.55	ND	ND	ND	ND
Dibenzo[a,h]anthracene	ND-2.21	1.11	ND	ND	ND	ND	ND-2.00	1.00	ND	ND	ND	ND
Benzo[g,h,i]perylene	ND-2.22	1.11	ND	ND	ND -0.10	0.05	0.12-1.26	0.69	ND-1.24	0.62	ND-1.57	0.79
Total PAHs (∑PAHs)	2.97-28.66	15.82	1.70-3.85	2.78	4.10-20.33	12.22	5.23-20.54	12.89	2.44-12.70	7.57	2.89-18.80	10.85

Table 3. Minimum, maximum, and mean concentrations of PAHs (ng/g), and the detection frequencies in crabs.

PAHs	Rings	Minimum conc	Maximum conc	Mean ± SD conc	Detection Frequency (%)
Naphthalene	2	ND	3.31	1.29 ± 1.24	83.3
Acenapthylene	3	0.05	2.41	0.78 ± 0.84	100
Fluorene	3	ND	3.09	1.01 ± 1.07	91.7
Anthracene	3	0.30	3.12	1.30 ± 0.99	100
Benzo[a]anthracene	4	0.27	5.40	2.16 ± 1.80	100
Benzo[k]fluoranthene	5	0.08	2.64	0.84 ± 0.89	100
Benzo[a]pyrene	5	0.02	2.43	0.78 ± 0.89	100
Benzo[b]fluoranthene	5	ND	2.91	1.08 ± 1.10	91.7
Indeno[1,2,3-cd]pyrene	6	ND	1.09	0.22 ± 0.37	33.3
Dibenzo[a,h]anthracene	5	ND	2.21	0.35 ± 0.82	16.7
Benzo[g,h,i]perylene	6	ND	2.22	0.54 ± 0.80	50.0
∑PAHs		**1.70**	**28.66**	**10.35 ± 3.44**	100

the samples, respectively, and their concentrations were up to 2.22 ng/g. The highest concentrations of most of the PAHs (nine out of eleven) were recorded in crabs from Wesha. The highest concentrations of benzo[a]anthracene and indeno[1,2,3-cd]pyrene were found in samples from Bumbwini Makoba and Ngezi, respectively. Generally, the concentrations of the PAHs recorded from Jozani crabs were the lowest.

SD = Standard deviation; ND = Not detected

The total concentrations of the PAHs in crab samples varied among the sampling sites. Low molecular weight PAHs were found in samples from most of the sites, while some high molecular weight PAHs like dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene and benzo[g,h,i]perylene were not found in samples from most of the sites. Total PAHs concentrations ranged from 1.70 to 28.66 ng/g. The highest concentrations measured in crabs at Wesha were probably due to oil spills and other anthropogenic activities near the coastal area. The coastal area of Wesha was formerly the site where diesel powered electric generators operated, and currently has an oil depot, which could be the source of contamination of the mangrove ecosystems. Similar results were reported by Ekpo *et al.* (2012) who investigated PAHs contamination and accumulation in the mangrove ecosystem in the Niger Delta. These authors associated PAHs contamination and accumulation in the Niger Delta with petroleum-related activities. Wesha mangrove ecosystem receives contamination of PAHs from both petrogenic and pyrogenic sources. The possible sources of contamination at Wesha station include day-to-day shipping operations and road smelters. Crab samples from Jozani were observed to have the lowest concentrations of PAHs in this study. This is due to low anthropogenic activities in this protected area.

PAHs Profiles in Crabs

The PAHs trend in crab samples showed relatively higher concentrations of low molecular weight PAHs of two to four benzene rings than the high molecular weight PAHs of five to six rings. The dominant compounds were benzo[a]anthracene (four rings) followed by anthracene (three rings) and benzo[b]fluoranthene (five rings). Indeno[1,2,3-cd]pyrene (six rings) showed the lowest concentrations. The findings of low molecular weight PAHs of two to four aromatic rings in crab samples observed in this study could be related to pyrogenic anthropogenic activities, like domestic emissions. Crabs could be exposed to higher concentrations of low molecular weight PAHs than the high molecular weight PAHs because the low molecular weight PAHs are relatively more soluble in the water column compared to the high molecular weight PAHs. Therefore low molecular weight PAHs are more bioavailable despite being less tightly bound to the organic matter in sediments (Eickhoff *et al*., 2003).

Table 4. Concentrations of PAHs in sediment samples (ng/g dry weight).

Sampling site	Wesha		Jozani		Kinazini		Ngezi	
No. sampling points	3		3		3		3	
PAHs/category	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Min	Mean ± SD
Naphthalene	2.99-4.03	3.40 ± 0.55	3.21-3.34	3.26 ± 0.07	3.63-8.30	5.79 ± 2.35	3.51-4.35	3.89 ± 0.43
Acenaphthylene	1.78-2.84	2.26 ± 0.54	2.17-2.38	2.25 ± 0.11	2.30-4.13	3.28 ± 0.92	1.74-3.45	2.34 ± 0.97
Fluorene	2.37-3.41	2.87 ± 0.52	2.79-3.73	3.11 ± 0.54	2.95-6.69	5.04 ± 1.91	2.73-5.40	3.63 ± 1.53
Anthracene	2.35-3.15	2.73 ± 0.40	2.54-3.00	2.82 ± 0.25	5.56-8.04	7.07 ± 1.32	2.12-3.39	2.60 ± 0.69
Benzo[a]anthracene	2.88-3.94	3.31 ± 0.56	ND-2.59	1.68 ± 1.46	8.45-8.68	8.53 ± 0.13	1.92-2.73	2.35 ± 0.41
Benzo[k]fluoranthene	2.10-3.75	2.74 ± 0.88	1.93-2.38	2.19 ± 0.23	8.93-9.51	9.15 ± 0.31	1.64-2.14	1.97 ± 0.29
Benzo[a]pyrene	1.89-2.87	2.39 ± 0.49	2.02-2.24	2.11 ± 0.12	6.54-7.12	6.83 ± 0.29	1.57-7.65	3.75 ± 3.39
Benzo[b]fluoranthene	2.35-3.33	2.74 ± 0.52	1.99-2.10	2.04 ± 0.06	8.40-8.93	8.63 ± 0.27	1.63-2.10	1.90 ± 0.24
Indeno[1,2,3-cd]pyrene	2.81-3.55	3.28 ± 0.41	2.14-2.19	2.16 ± 0.03	10.40-11.90	11.28 ± 0.78	1.70-2.47	2.06 ± 0.39
Dibenzo[a,h]anthracene	1.88-2.93	2.38 ± 0.53	1.96-2.04	2.00 ± 0.04	3.05-3.96	3.53 ± 0.46	ND-1.75	0.58 ± 1.01
Benzo[g,h,i]perylene	ND-2.38	1.43 ± 1.26	ND-2.14	1.42 ± 1.23	6.58-8.06	7.56 ± 0.85	ND-1.98	1.19 ± 1.05
∑PAHs	26.20-33.78	29.52 ± 3.88	21.95-26.87	25.04 ± 2.70	67.02-81.94	76.70 ± 8.40	20.14-31.78	26.26 ± 5.84

The total PAHs levels from edible crab tissues obtained in this study were much lower than the levels reported by other authors for crabs in highly contaminated areas. For instance, Mostafa (2002) found concentrations ranging from 1318.6 to 3767.4 ng/g for total PAHs in crabs from Lake Timsah, while Ekpo *et al.* (2012) reported mean total PAHs levels of 29325.1 ng/g ww in crabs from the Calabar River, Niger delta. The mangrove ecosystems of Zanzibar coastal areas are less impacted by anthropogenic activities compared with those areas studied by Mostafa (2002) and Ekpo *et al.* (2012).

PAHs in Sediment Samples

PAHs Detection and Concentrations in Sediments

The PAHs concentrations in the sediment samples are shown in Table 4 and the levels and detection frequencies in sediments are summarised in Table 5. Total PAHs concentrations in sediments ranged from 20.14 to 81.94 ng/g dw. PAHs were detected in most sediment samples with concentrations for individual compounds up to 11.90 ng/g. The highest concentrations of most PAHs in sediment samples were detected at Kinazini. Kinazini is a commercial area from which there is direct release of domestic wastes and municipal wastewater to the mangrove ecosystem. Boat making and servicing and oil spills from service stations and other products of anthropogenic activities could be contributing to the contamination in this area. Kinazini receives contamination from domestic sewage from the urban area especially through the stream which passes through the area. Ngezi is a government preserved area and there are low anthropogenic activities within this area. However, the area receives contamination from nearby areas probably due to forest fire and agricultural burning, which contribute to the levels of PAHs found. PAHs are also known to be synthesised by some higher plants, microorganisms and some animals (Eisler, 1987; Mohanraj & Azeez, 2003).

The concentrations of the PAHs detected in sediments during this study are comparable to the results obtained for PAHs levels from the Niger Delta which ranged from 0.1 to 28 ng/g (Anyakora *et al*., 2005).

PAHs Profiles in Sediments

The results suggest that both petrogenic and pyrogenic sources contributed to the contamination of the sediments in the study areas since both high and low molecular weight PAHs were found in the sediment samples. The nature of contamination sources controls the molecular distribution of the PAHs, although there are other factors like photo-oxidation, biodegradation, evaporation and dissolution that lead to degradation of specific compounds that also affect the pollutants distribution (Neff, 1979). Generally, the low molecular weight PAHs were found to be in low percentage concentrations in sediment samples

Table 4 (Ctd). Concentrations of PAHs in sediment samples (ng/g dry weight).

Sampling site		**Mbweni**		**Maruhubi**	**B. Makoba**		**Donge Muwanda**
No. sampling points		**3**		**3**	**2**		**3**
PAHs/category	**Range**	**Mean ± SD**	**Range**	**Mean ± SD**	**Mean**	**Range**	**Mean ± SD**
Naphthalene	2.32-3.49	2.89 ± 0.59	2.42-3.21	2.92 ± 0.43	2.66	3.31-5.32	4.02 ± 1.13
Acenaphthylene	1.60-2.52	2.09 ± 0.46	1.69-2.26	2.01 ± 0.29	1.74	1.53-2.68	2.14 ± 0.58
Fluorene	2.59-3.12	2.94 ± 0.31	3.14-4.82	3.90 ± 0.85	2.81	2.17-3.95	2.97 ± 0.90
Anthracene	2.05-3.02	2.68 ± 0.54	2.63-4.33	3.26 ± 0.93	2.40	2.18-4.99	3.37 ± 1.46
Benzo[a]anthracene	2.42-2.57	2.52 ± 0.08	2.65-2.92	2.77 ± 0.14	2.34	2.58-4.73	3.67 ± 1.08
Benzo[k]fluoranthene	1.69-2.54	2.15 ± 0.43	2.20-2.58	2.39 ± 0.19	1.81	2.52-3.66	3.17 ± 0.59
Benzo[a]pyrene	1.63-2.20	1.99 ± 0.32	2.10-2.29	2.18 ± 0.10	1.69	2.25-3.03	2.66 ± 0.39
Benzo[b]fluoranthene	1.77-2.21	2.05 ± 0.24	2.26-2.52	2.35 ± 0.14	1.87	2.31-3.86	3.04 ± 0.78
Indeno[1,2,3-cd]pyrene	2.16-2.23	2.20 ± 0.04	2.41-2.79	2.54 ± 0.21	2.22	2.43-3.86	3.24 ± 0.73
Dibenzo[a,h]anthracene	1.48-1.98	1.80 ± 0.28	1.75-1.99	1.83 ± 0.14	1.50	1.29-2.35	1.88 ± 0.54
Benzo[g,h,i]perylene	1.55-2.10	1.91 ± 0.31	1.82-2.13	1.99 ± 0.16	1.51	2.00-2.68	2.44 ± 0.38
∑PAHs	21.32-27.17	25.22 ± 3.38	26.72-30.77	28.17 ± 2.26	22.54	27.45-38.39	32.59 ± 5.50

Table 5. Minimum, maximum, and mean concentrations of PAHs (ng/g), and the detection frequencies (%) in sediments samples.

PAH	Minimum conc	Maximum conc	Mean ± SD	Detection Frequency (%)
Naphthalene	2.32	8.30	3.69 ± 1.29	100
Acenaphthylene	1.53	4.13	2.31 ± 0.66	100
Fluorene	2.17	6.69	3.46 ± 1.15	100
Anthracene	2.05	8.04	3.45 ± 1.67	100
Benzo[a]anthracene	ND	8.68	3.49 ± 2.22	95.5
Benzo[k]fluoranthene	1.64	9.51	3.32 ± 2.44	100
Benzo[a]pyrene	1.57	7.65	3.07 ± 1.96	100
Benzo[b]fluoranthene	1.63	8.93	3.19 ± 2.27	100
Indeno[1,2,3-cd]pyrene	1.70	11.90	3.75 ± 3.12	100
Dibenzo[a,h]anthracene	ND	3.96	1.98 ± 0.92	90.9
Benzo[ghi]perylene	ND	8.06	2.52 ± 2.21	86.4
∑PAHs	**20.14**	**81.94**	**34.23± 6.45**	100

while the high molecular weight PAHs were found to be in high percentages. Some low and high molecular weight PAHs showed similar dominance in sediment samples. This is due to the relatively higher hydrophobic and lipophilic characteristics of high molecular weight PAHs, which make them less soluble in water and likely to settle to the bottom of the aquatic environment and bind tightly to the organic matter in sediments (Sakari, 2012). The concentrations of PAHs in sediments observed from this study were due to the hydrophobicity of the PAHs which allows them to easily adsorb to the sediments (Deschenes *et al*., 1996; Karthikeyan & Bhandari, 2001).

Comparison of PAHs Concentrations in Crabs and Sediments

The results showed that there was no significant correlation between the concentrations of total PAHs in crabs and sediments (r = 0.2103, df = 22, p = 0.5347). This indicated that the crabs are exposed to PAHs from various sources such as water. Generally, the samples collected near to the mangrove ecosystem (upper samples) had the highest concentrations of PAHs (mean = 3.50 ng/g), followed by middle samples (mean = 3.30 ng/g), and the lower samples collected nearest to the sea-line had the lowest concentrations (mean = 2.74 ng/g). This is due to the characteristics of the mangroves to trap organic materials from the water column where the PAHs can bind tightly (Sanders *et al.*, 2010). However, the results from ANOVA showed that there were no significant differences in the PAHs concentrations in sediments among the upper, middle and lower sections of the sampling locations for most sites (F (2,30) = 0.9491 – 2.542, p = 0.0955 – 0.398), which suggested even distribution of the contaminants. There were significant differences in the PAHs concentrations in sediments among the upper, middle and lower sections of the sampling locations at Mbweni (lower < middle and upper; F (2, 30) = 5.563, p = 0.0088) and Donge Muwanda (lower < middle and upper; F (2, 30) = 3.689, p = 0.037). This could be attributed to the differences in sediment composition among the locations of the mangrove stands, leading to differences in trapping of PAHs. The concentrations of the PAHs in sediments were significantly greater than the concentrations in crabs (t = 4.279 at df = 32, p = 0.002). This is due to the fact that sediments act as reservoirs or sinks, and therefore tend to accumulate more contaminants.

Evaluation of PAHs Contamination in Mangrove Ecosystems in Zanzibar

The data from the present study were compared with the data reported in the literature for the maximum permitted levels of PAHs in crabs for food safety (European Commission, 2011). The maximum permitted level for benzo[a]pyrene is 2 ng/g ww while the cumulative permitted level for benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene and chrysene is 12 ng/g ww (European Commission, 2011). The crabs from Wesha were found to contain benzo[a]pyrene concentrations above the maximum permitted level

making them potentially harmful for consumption by human beings. The concentrations of individual PAHs in sediments from the coastal areas of Zanzibar did not exceed the Threshold Effect Level (TEL) and were below the Probable Effect Level (PEL). PEL is the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects, and TEL is the upper limit of the range of sediment contaminant concentrations that is associated with no effect. The TEL for naphthalene is 34.6 ng/g, other TELs are 5.87 ng/g for acenaphthylene, 113 ng/g for fluorene, 46.9 ng/g for anthracene, 74.8 ng/g for benzo[a]anthracene, 88.8 ng/g for benzo[a]pyrene, 6.22 ng/g for dibenzo[a,h]anthracene, and 108 ng/g for chrysene. The PEL for these compounds range from 128 to 1494 ng/g (MacDonald, 1994).

Conclusions

All the crab and sediment samples from the mangrove ecosystems in the Zanzibar Islands coastal areas were found to be contaminated with various types of PAHs, which could be related to pyrogenic and petrogenic sources, among others. The total concentrations of PAHs in crab tissues were up to 28.66 ng/g fw, while the highest concentration of total PAHs in sediment samples was 81.94 ng/g dw. The levels of the PAHs in crabs were lower than the PAHs levels in sediments. In sites with high anthropogenic activities like Kinazini, the level of contamination in sediments was higher than in areas with low anthropogenic activities. The levels of contamination were generally low, except in crabs from one site (Wesha).

Acknowledgements

This study was supported by the Tanzania Commission for Science and Technology (COSTECH).

References

Anyakora C, Ogbeche A, Palmer P, Coker H, Ukpo G, Ogah C (2005) GC/MS analysis of polynuclear aromatic hydrocarbons in sediment samples from the Niger Delta region. Chemosphere 60: 990-997

Deschenes L, Lafrance P, Villeneuve JP, Samson R (1996). Adding sodium dodecyl sulfate and *Pseudomonas aeruginosa* UG2 biosurfactants inhibits polycyclic aromatic hydrocarbon biodegradation in a weathered creosote-contaminated soil. Applied Microbiology and Biotechnology 46: 638-646

European Commission (2011) Commission Regulation (EU) No 835/2011, Amending Regulation (EC) No 1881/2006 as regards maximum levels for polycyclic aromatic hydrocarbons in foodstuffs, European Union

Eickhoff CV, He SX, Gobas FAPC, Law FC (2003) Determination of polycyclic aromatic hydrocarbons in dungeness crabs (*Cancer magister*) near an aluminium smelter in Kitimat Arm, British Columbia, Canada. Environmental toxicology and Chemistry 22: 50-58

Eisler R (1987) Polycyclic aromatic hydrocarbon hazards to fish, wildlife and invertebrates. A synoptic review: Laural, Md., Patuxent Wildlife Research Centre, U.S Fish and Wildlife Service, Biological Report 85, 81 pp

Ekpo BO, Ita OEO, Offem JO, Adie PA (2012) Anthropogenic PAHs in sediment-dwelling biota from mangrove areas of the Calabar River, SE Niger Delta, Nigeria. Environment and Natural Resources Research 2 (4): 89-100

Eljarrat E, Barcelo D (2003) Priority lists for persistent organic pollutants and emerging contaminants based on their relative toxic potency in environmental samples. TrAC- Trends in Analytical Chemistry 22: 655-665

Gaspare L, Machiwa JF, Mdachi SJM, Streck G, Brack W (2009) Polycyclic aromatic hydrocarbon (PAH) contamination of surface sediments and oysters from the intertidal areas of Dar es Salaam, Tanzania. Environmental Pollution 157: 24-34

Kanaly RA, Harayama S (2000). Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons by bacteria. Journal of Bacteriology 182: 2059-2067

Karthikeyan R, Bhandari A (2001) Anaerobic biotransformation of aromatic and polycyclic aromatic hydrocarbons in soil microcosms: a review. Journal of Hazardous Substance Research 3: 1-19

Macdonald DD (1994) Approach to the assessments of sediment quality in Florida Coastal waters. Florida Department of Environmental Protection, Tallahassee, Florida.

Mohanraj R, Azeez PA (2003) Polycyclic aromatic hydrocarbons in air and their toxic potency. Resonance 8: 20-27

Mostafa GA (2002) Monitoring of polycyclic aromatic hydrocarbons in seafoods from Lake Timsah. International Journal of Environmental Health Research 12: 83-91

Motulsky H (1998) GraphPad Software, Instat Guide to Choosing and Interpreting Statistical Tests, GraphPad Software, Inc. San Diego, California, USA

Nasr IN, Arief MH, Abdel-Aleem AH, Malhat FM (2010) Polycyclic aromatic hydrocarbons (PAHs) in aquatic environment at El Menofiya Governorate, Egypt. Journal of Applied Sciences Research 6: 13-21

Neff JM (1979) Polycyclic aromatic hydrocarbons in the aquatic environment. Sources, fates and biological effects. Applied Sciences 262

Sanders CJ, Smoak JM, Naidu AS, Sanders LM, Patchineelam SR (2010) Organic carbon burial in a mangrove forest, margin and intertidal mud flat. Estuarine, Coastal and Shelf Science 90: 168-172

Sakari M (2012) Depositional history of Polycyclic Aromatic Hydrocarbons: reconstruction of petroleum pollution records in Peninsular Malaysia. In: Puzyn T, Mostrag A (eds) Organic pollutants ten years after Stockholm Convention – Environmental and Analytical Update, INTECH Open Access Publisher