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Characterization and Source Assessment of Heavy Metals and Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments of the Fosu Lagoon, Ghana

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The first results ever obtained on polycyclic aromatic hydrocarbon (PAHs) concentrations in the Fosu lagoon surface sediments are presented together with corresponding heavy metal (Fe, Mn, Cd, Zn and Ni) concentrations. Samples collected on a monthly basis from November 2003–April 2004 (Heavy metals) and December 2003–January 2004 (PAHs) at 8 locations, representing different anthropogenic sources of contamination to the lagoon, were analyzed. Concentrations of Cd and Ni in the lagoon sediment suggest greater contamination to the lagoon from industrial activities in the vicinity of the lagoon; 50% of the sediment samples exceeded some established sediment Cd guidelines for the protection of aquatic lives. Then, 15 PAHs were detected among the sediments from the different locations and the compositional pattern in decreasing order was 3-ring > 5-ring > 4-ring > 6-ring > 2-ring PAH compounds. Σ PAH concentrations in the sediment samples ranged from 254 to 558 mg/kg, with a mean of 359.4 mg/kg. Two distinct areas were identified to be a major source of anthropogenic load of both heavy metals and PAH; the mechanical shop in the northeastern sector of the lagoon is the main location for the input of Cd and its associated PAH compounds (e.g., acenaphthylene, acenaphthene, naphthalene and benzo[a]fluoranthene) and to a lesser extent Ni. Both combustion and petroleum sources may account for PAH loads from this

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area. The residential area in the northern sector is responsible for high loads of Mn and its associated PAH compounds (e.g., phenanthrene, benzo[a]pyrene and anthracene). These chemicals seem to enter the lagoon mainly by the combustion of especially wood or coal.

Key Words: Heavy metals; PAHs; Fosu lagoon; Sediments; Ghana; Pollution.

INTRODUCTION

The coastline of Ghana, which forms part of the Gulf of Guinea, is dotted with about 90 lagoons.^[1] There are two main types: the “open” and the “closed” types. The former is always opened to the sea and is associated with rivers that flow all year round, while the latter remains closed to the sea for most part of the year.^[1–3] The quality of both types, particularly the “closed,” of which Fosu lagoon is an example, is often influenced by activities inland and serve as traps for materials brought from inland as a result of flocculation, precipitation and sedimentation or by careless direct waste disposal into the lagoon. Cape Coast is expanding in population and due to poor waste management in the municipality, the lagoon has been a receiving sink for most domestic and municipal waste.

Furthermore, the recent implementation of structural adjustment programs (SAPs) in Ghana has had a concomitant shift from the formal/modern sector to the informal sectors (i.e., small scale private enterprises engaging in a wide variety of economic activities) and may have its consequential environmental impact.^[4] Cape Coast is one of such coastal cities in the country where small-scale informal sector activities are denominating its economic base. These informal ventures are, however, poorly regulated and usually are involved in careless disposal of waste. Most of the activities are within the vicinity of the Fosu lagoon (the main lagoon in Cape Coast), which of recent times has experienced considerable changes that include pollution and degradation of the watershed.^[5–7] Once upheld for the catch of delicious tilapia (*Tilapia courier*) and crabs, the lagoon is now noted for routine dryness, frequent inversion of weeds, foam covering surfaces and domestic waste dumps. Until a recent intervention by the Environmental Protection Agency-EPA (Ghana), the lagoon was also infested with mansonias mosquitoes, which causes elephantiasis.^[7] The causes of these changes to the lagoon have not been well defined, but almost certainly are associated to the increasing population growth and developmental activities in the municipality. The population in Cape Coast between 1984 and 2000, for instance, increased by approximately 25% (i.e., from 65,763 to 82,291) and there are clear indications of further increase since the last population census in Ghana.^[8]

Despite the drastic negative impact, an up-to-date chemical data is still lacking on the lagoon. The limited available data in the literature are valuable,

but were typically investigated over two decades ago and are limited only to water columns. They are also not inclusive of various classes of chemicals; being limited to only some physicochemical parameters (e.g. pH, BOD, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , PO_4^{2-} -P, NH_4^+ -N, Cl^- , F^- and NO_3^- -N, SO_4^{2-} and HCO_3^-).^[3, 9, 10] Current activities in the surrounding areas of the lagoon suggest polycyclic aromatic hydrocarbons (PAHs) and heavy metals as two other classes of chemicals that are likely to pollute the lagoon. Many PAH compounds are carcinogens and the tendency of heavy metals to bioaccumulate makes both dangerous to aquatic lives in the lagoon, and to humans through the food chain. In view of their toxic nature, the knowledge of the sources and fate of these compounds in the environment is very important. Industrial activities, fossil fuel combustion, vehicle washing, and waste incineration (all of which currently occur in the vicinity of the lagoon) are known anthropogenic sources of PAHs.^[11, 12] Heavy metal pollution may also arise from waste pigments, paints and crude oils, overused batteries, leached metals from garbage and solid waste dumps, and rusted metallic objects,^[13] all of which are carelessly disposed into the lagoon. In spite of these facts, no data are as yet available on PAHs in any environmental medium of the lagoon, and heavy metal data are still scant.

PAHs are incorporated into bottom sediments, primarily by removal from the water column through their association with particulate matter.^[11] A variety of aquatic organisms also live in contact with bed sediments, thus making sediments important exposure route for these organisms to PAHs. In estuarine ecosystems, sediments are an important sink of metals and may also serve as an enriched source of metals for benthic organisms.^[14, 15] In the Fosu Lagoon most fish have been noted to depend on the sediment for their food.^[16] Bed sediment heavy metal concentrations are also more reliable indicators of water pollution than the water concentrations, which fluctuate by several orders of magnitude over short periods.^[17]

About a decade ago, Dodoo and Adjei (1995) investigated the heavy metal pollution in the sediments of the Fosu Lagoon and observed significantly high concentrations at certain points on the lagoon adjacent to human settlements, but only copper and zinc were measured.^[18] There have since been various new and increased activities in the area and hence the need to expand such sediment chemistry studies to include other currently relevant heavy metals and compounds likely to occur in the lagoon. This current study focuses on investigating and assessing the current level of Cd, Ni, Zn, Mn and Fe and various PAH compounds in the Fosu Lagoon to establish baseline data for these chemicals in the sediments of the lagoon due to present anthropogenic activities and to determine the sources of these chemicals to the lagoon. It is intended that the results will help in the implementation of environmental sustainable policies for effective water pollution control and management of the lagoon.

MATERIAL AND METHODS

The Study Area

Fosu Lagoon (Fig. 1) is one of the many lagoons along the Gulf of Guinea in the ancient city of Cape Coast, Ghana in West Africa. Cape Coast lies along the Atlantic Ocean and is on the longitude 1° 15' West of the Greenwich Meridian

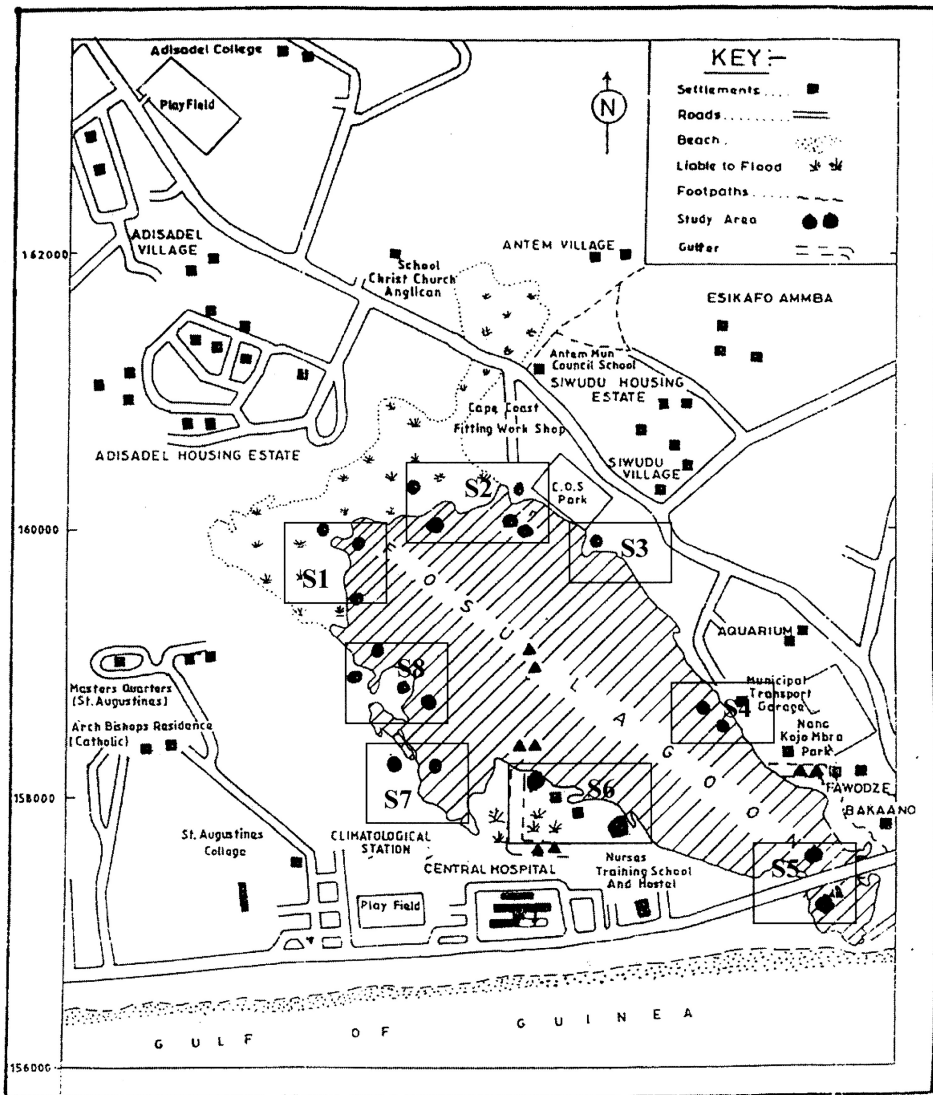


Figure 1: Map showing points sampled on the Fosu Lagoon.

and the latitude 5° 5' North of the Equator. It is an important tourist and educational town, having many of the country's finest and oldest secondary schools and one university. As this city lies in the belt of tropical and equatorial climates, temperatures are high, ranging between 25°C and 35°C with little variation through the years. There are two wet seasons in a year, the major one from April to July and a minor season from September to November. Across the country, the dry dusty Harmattan wind blows from the northeast from December to March, lowering the humidity. In the study area, the effects are felt most in January.

Fosu Lagoon is surrounded by many sites that can act as point sources for discharge of pollutants (Fig. 1). These include domestic waste discharges from a highly populated residential area in the northern side of the lagoon; industrial waste discharge from a cluster of mechanical workshops on the North Eastern side and a Municipal Transport Garage on the Eastern side; a direct discharged untreated laboratory and hospital effluents respectively from a college and a hospital on the Western and South Western section of the lagoon; and domestic effluents and sewage inputs from the southern end.

The human activity in the study area is so great that eutrophication has caused massive sedimentation and especially, in the more populated northern sector, one can walk many meters on waterweeds through the lagoon. Also in the western and southwestern sector, some portions of the lagoon have been transformed into waste and marshland.

Sample Collection

The samples investigated in this work were sediment samples from the Fosu Lagoon collected monthly from November 2003 to April 2004. Typically, three samples were collected for the particular sampling month as follows: within the first week, approximately the middle of the month and within the last week of the month. Sampling was done at various points of the lagoon where refuse and other effluents are discharged. Typically, the sampling locations were less than 50 m from the respective refuse dumping sites or effluent entry point for the different areas/activities around the lagoon. The sample sites were thus presumed as the discharge points for the corresponding areas (see Fig. 1) as follows: Ola-North—a residential area (S1), Siwudu—a cluster of mechanical/fitting shops (S2), Robert Mensah Sports Stadium—a recreational centre (S3), a municipal automobile garage (S4), Baakano—an estuary with lots of refuse dumping activities (S5), a district hospital (S6) and an educational institution—St Augustine's College—where laboratory effluent enters the lagoon (S7). Another sample from the college (S8) was taken; but at a site where less anthropogenic effluence is expected. Teflon-coated soil auger was used to collect the sediment samples (~160 to 200 g) at an average depth of 30 cm into clean, wide-necked amber glass containers with screw

caps and lids lined with aluminum foil. The samples were then refrigerated (at temperatures between -5 and 4°C) prior to being analyzed.

Sample Preparation and Chemical Analysis

In the laboratory, the soil samples collected (typically 3 per sampling month) from each sampling station were freed from pieces of roots, pebbles and other foreign objects. The samples were then air dried to a constant weight, ground and homogenized in a porcelain mortar and sieved with a $90\text{-}\mu\text{m}$ mesh as a composite sample for the site. The final composite samples weighed typically between 4 to 10 g.

Heavy Metals. Two replicate of air-dried homogenized samples for each site were acid digested for the determination of metal by the following procedure. Then, 10 ml 1:1 nitric acid was added to 1.0 g sample in a flat bottom flask. The slurry formed was well mixed, covered with a watch glass, and refluxed for 10–15 minutes without boiling. It was then allowed to cool and 10 ml conc. HNO_3 added and refluxed further for 1 hour. The solution was then allowed to evaporate to 5 ml without boiling on a hot plate, cooled and 2 ml doubly distilled water and 3 ml 30% v/v hydrogen peroxide added. The content was covered and warmed with drop-wise additions of 30% v/v hydrogen peroxide until the effervescence was minimal but not more than a total of 10 ml of 30% v/v hydrogen peroxide was added. Then, 5 ml conc. HCl and 10 ml double distilled water were added to the cooled solution and further refluxed for 15 minutes. It was cooled, filtered and diluted to 100 ml in a volumetric flask with double distilled water for immediate analysis or otherwise stored in Teflon bottles in a refrigerator (-5 to 4°C) for analysis as soon as practical.^[19] Duplicate readings were performed on each composite sample for each studied metal.

The Shimadzu flame Atomic Absorption Spectrophotometer model No. 6010 was employed in the determination of zinc (Zn), cadmium (Cd), nickel (Ni), manganese (Mn) and iron (Fe) using the air–acetylene flame. Calibration was performed by analyzing a reagent blank sample and standard solutions within 0.5 to 2.0 ppm. Accurately weighed analytical grade reagents of the respective metal ions were similarly digested as described above to prepare known concentrations of the metal ions to serve as reference materials and AAS used to perform recovery analysis as a check on the accuracy of the method. As can be seen in Table 1, heavy metal recoveries were satisfactory as proved by the analysis of the reference materials.

Polynuclear Aromatic Hydrocarbons (PAHs). Fifteen PAH compounds were identified and analyzed in the sediment samples as follows: naphthalene (NA), acenaphthylene (Ayl), acenaphthene (Ac), fluorene (F), carbazole (Carb), phenanthrene (Phen), anthracene (An), fluoranthene (Fl), pyrene (Py), benzo [a]anthracene (BaA), chrysene (Ch), benzo [a] fluoranthene (BaFl), benzo [a] pyrene (BaP), perylene (Pyl) and benzo [g,h,i] perylene (BghiPl).

Table 1: Results of recovery and reproducibility studies determined reference samples of Zn, Cd, Mn, Fe and Ni).

| Metal | Reference concentration (mg/L) | Our measured mean value (mg/L) | Standard deviation (n =3) | % Recovery |
|-----------|--------------------------------|--------------------------------|---------------------------|------------|
| Zinc | 0.20 | 0.21 | 0.02 | 105 |
| | 0.40 | 0.39 | 0.01 | 97.5 |
| | 0.80 | 0.78 | 0.00 | 97.5 |
| | 1.00 | 1.00 | 0.03 | 100 |
| Cadmium | 0.20 | 0.19 | 0.00 | 95 |
| | 0.40 | 0.40 | 0.02 | 100 |
| | 0.80 | 0.79 | 0.02 | 98.8 |
| | 1.00 | 0.98 | 0.00 | 100 |
| Manganese | 0.20 | 0.19 | 0.00 | 95 |
| | 0.40 | 0.40 | 0.02 | 100 |
| | 0.80 | 0.79 | 0.02 | 98.8 |
| | 1.00 | 0.98 | 0.00 | 100 |
| Iron | 0.20 | 0.21 | 0.02 | 105 |
| | 0.40 | 0.39 | 0.01 | 97.5 |
| | 0.80 | 0.78 | 0.00 | 97.5 |
| | 1.00 | 1.00 | 0.03 | 100 |
| Nickel | 0.20 | 0.19 | 0.00 | 95 |
| | 0.40 | 0.40 | 0.02 | 100 |
| | 0.80 | 0.79 | 0.02 | 98.8 |
| | 1.00 | 0.98 | 0.00 | 100 |

The samples were spiked with a deuterated PAH surrogate recovery standard solution (i.e., deuterated p-terphenyl), homogenized and soxhlet-extracted with dichloromethane for 6 hours. The extracts were concentrated by evaporating the dichloromethane solvent with a rotary evaporator. They were then subjected to column chromatographic purification by loading them onto silica gel/alumina column and eluting first with pentane followed by dichloromethane. The PAH content of the dichloromethane fraction was quantified by adding deuterated PAH internal standard solutions followed by gas chromatography-mass spectrometry (Hewlett Packard GCMS 5890 Series II) analysis. Naphthalene-d₈, acenaphathene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₀ and perylene-d₁₂ were found as suitable internal standards. Controls included reagent blanks and two certified reference soil materials (Environmental Agency).^[20] The GC-MS analyses were conducted at the Department of Geography and Environmental Sciences, University of Bradford, UK.

RESULTS AND DISCUSSION

There are no formal standards in Ghana for both inland and coastal sediment quality. However, in order to evaluate the likely toxicity resulting from the measured heavy metal and PAH contaminants in the lagoon, it is informative

to verify their compliance with known international, national or provincial standards. Simply as an arbitrary choice, the data obtained in this current investigation are being compared to Interim Canadian Sediment Quality Guidelines (ISQDs) established by the Canadian Council of Ministers of the Environment (CCME)^[11] and the Ontario (Canada) Ministry of Environment and Energy (OMOEE 1992)^[21] for the protection of aquatic life exposed to bed sediments. These guidelines are based on the probable effect levels (PELs)—i.e., concentration above which deleterious effects to organisms have been determined to occur^[11] and lowest effect levels (LEL) of concentrations, which indicate a level of sediment contamination at which a majority of benthic organisms are unaffected.^[21]

Heavy Metals

Environmental concerns pertaining to metals relate to their toxicity, the potential for bioaccumulation, and their associated hazards to human health and to aquatic life.^[22] Through the processes of precipitation and sedimentation, some heavy metals introduced in the aquatic system are adsorbed in the sediment. Sediments can thus provide useful information on the history of the water quality at a given location.^[23] The average heavy metal contents of the sediments samples over the study period for the eight anthropogenic sources (S1–S8) are presented in Figure 2 to Figure 6.

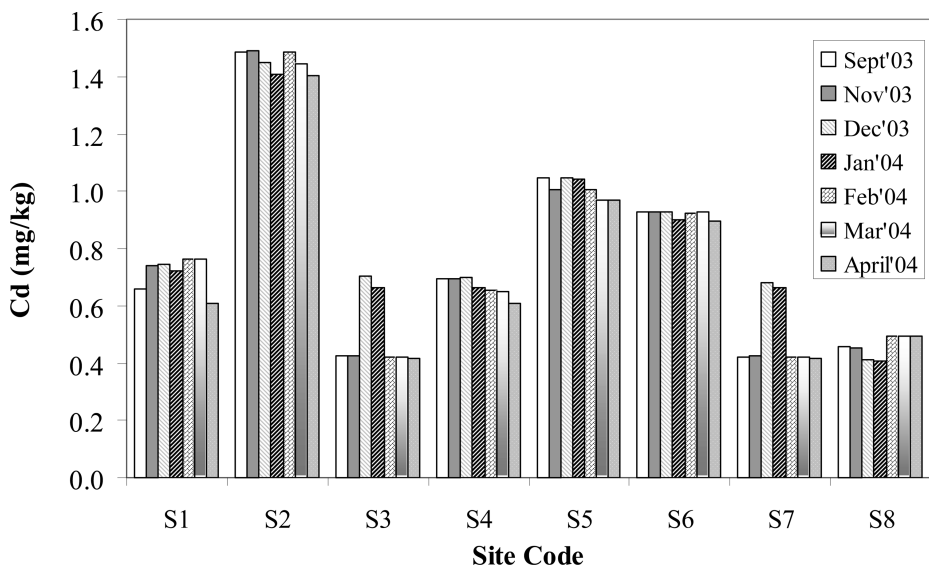


Figure 2: Cadmium concentrations in sediments from different anthropogenic sources in the Fosu Lagoon from September 2003 to April 2004.

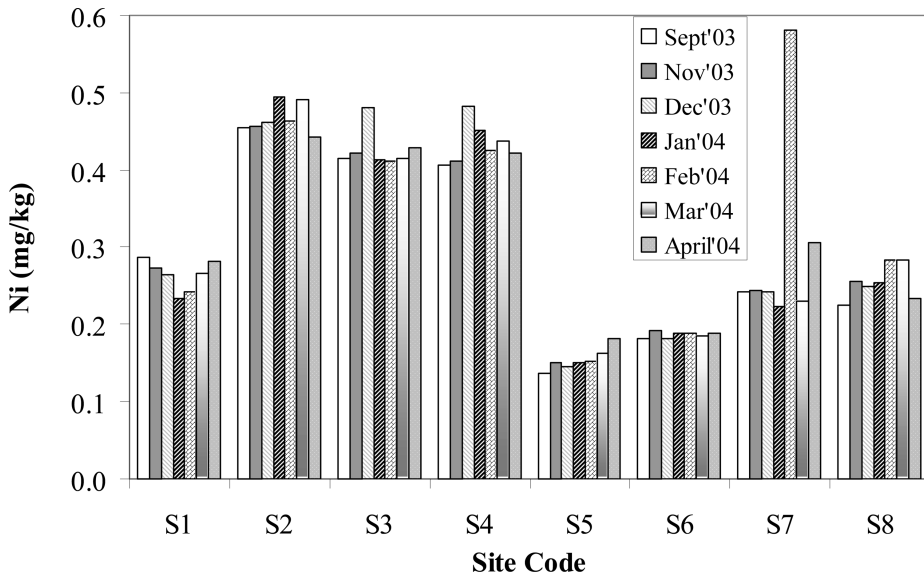


Figure 3: Nickel concentrations in sediments from different anthropogenic sources in the Fosu Lagoon from September 2003 to April 2004.

Cadmium. The sediment cadmium levels at the eight studies sites in the Fosu lagoon and for different months are shown in Figure 2. Whereas there was an extremely high site variation in Cd levels (95.9% total variation; $P < 0.0001$), differences between monthly data were not statistically significant

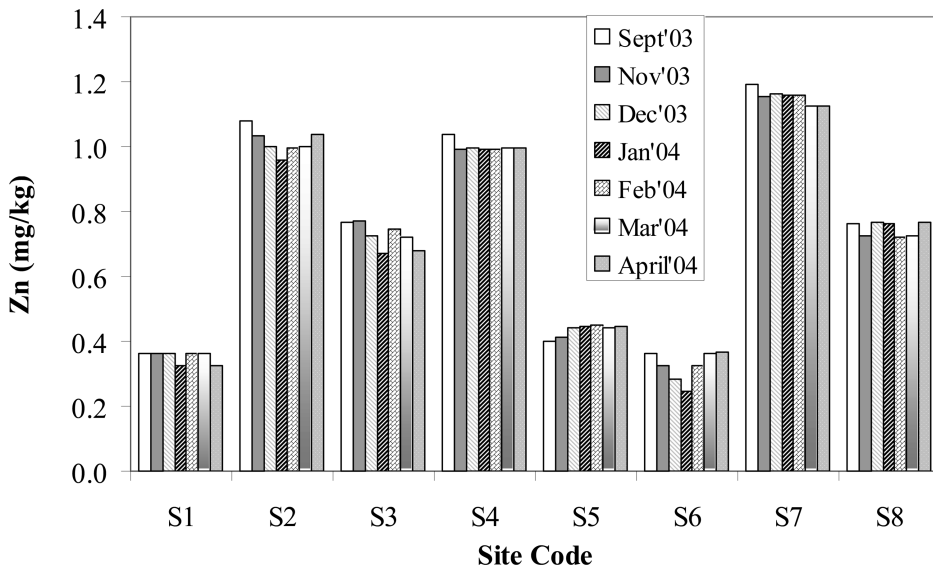


Figure 4: Zinc concentrations in sediments from different anthropogenic sources in the Fosu Lagoon from September 2003 to April 2004.

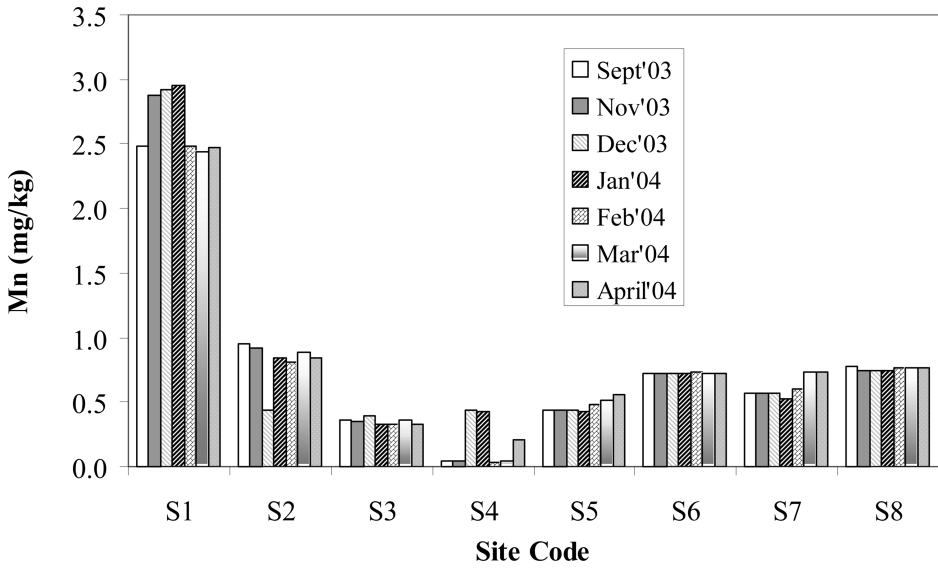


Figure 5: Manganese concentrations in sediments from different anthropogenic sources in the Fosu Lagoon from September 2003 to April 2004.

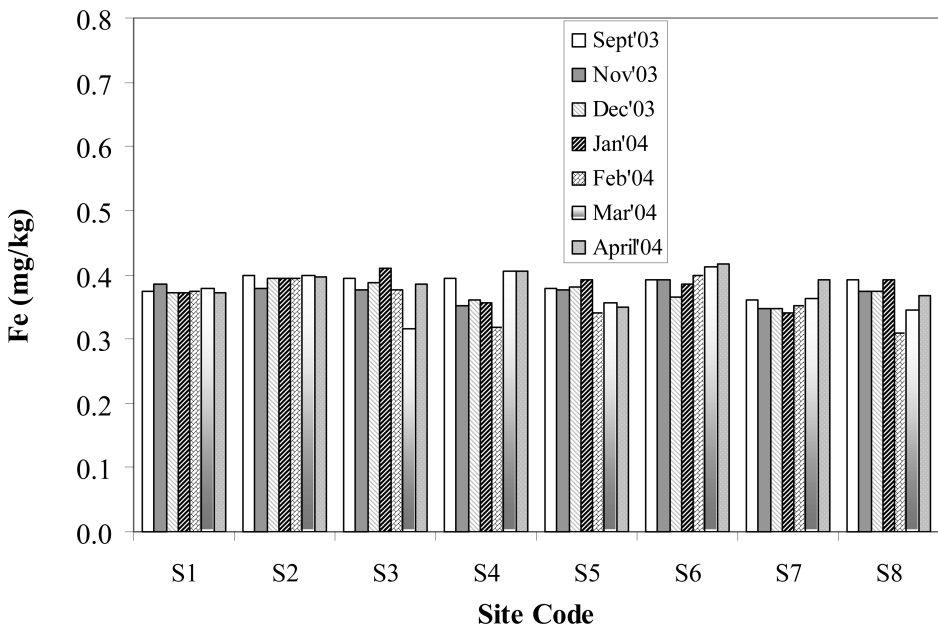


Figure 6: Iron concentrations in sediments from different anthropogenic sources in the Fosu Lagoon from September 2003 to April 2004.

(0.96% total variation; $P = 0.0681$) as shown by a two-way Anova test using the GraphPad Prism 4 for Windows XP 2000. S1 and S7, which are both close to recreational grounds, showed similar monthly trends ($R^2 = 0.997$) and exhibited significantly higher Cd concentration during the December and January survey periods ($\sim 39\%$ increases).

The general increasing trend for average Cd levels over the 8-month survey period is as follows: S8 (0.46 ± 0.04) < S7 (0.49 ± 0.12) \cong S3 (0.50 ± 0.13) < S4 (0.67 ± 0.03) < S1 (0.71 ± 0.06) < S6 (0.92 ± 0.01) < S5 (1.01 ± 0.03) < S2 (1.45 ± 0.04). As indicated earlier, S2 is a site where there is a cluster of mechanical/automobile fitting shops. Predominant industrial activities include car fittings, welding, painting, etc. Careless disposal of all kinds of waste from these activities into the lagoon is the norm in the locality. Disposal of waste from nickel/cadmium batteries, Cd-containing alloys, foils, oils, and electrical equipments are all possible sources of Cd to the lagoon. Also most drivers use this site, as their car washing base and that may be another likely source of Cd to the lagoon since most detergents contain Cd.

The site with the second highest record of Cd concentration was Site S5, which is in the southern sector of the lagoon, and it is uncertain whether the Cd origin or sediment chemistry at this site is different from site S2 or not. The southern segment of the lagoon receives huge amount of domestic effluents and sewage from nearby settlements, as well as leacheates of garbage and solid wastes dump through gutters. The relatively high prevalence of Cd distribution in this site seems to be mainly attributable to leaching of the metal from garbage and solid waste dumps. There are also other potential sources of Cd to the lagoon from this area, whose input may however be of a lesser extent. Atmospheric deposition from garbage incineration, volatile petroleum products from nearby filling stations, and smoke from vehicles may also contribute to Cd enrichment in sediments,^[11,24] although this was not examined. Near site S5 is a small bridge on the lagoon that serves as entry point for vehicles to or from Cape Coast and which usually have busy traffic. The possibility of inputs from some few mechanical/automobile activities in the southern part of the lagoon is also discussed next.

Cadmium distribution is lowest in site S8, where there are less industrial and commercial activities. S8 is one of the two St. Augustines, a secondary school point site area, which is mainly a residential area for the teachers and workers in the school. The place is sparsely populated and only few chemical wastes are expected to flow into the lagoon. Cadmium is a nonessential trace element that can be toxic to aquatic biota at elevated concentrations.^[11] The Canadian interim cadmium marine/estuarine sediment guideline for the protection of aquatic lives is 0.7 mg/kg and 50% of the samples analyzed from the lagoon showed exceedances to this guideline, with about an additional 20% only "marginally" meeting the guideline (i.e., between 0.6 to 0.7 mg/kg). All data collected for sites S2, S5, and S6 and almost all from S1 exceeded the

guideline. There is a significant variation between the sampling sites as far the sediment Cd concentration is concern ($CV = 43.7\%$). The mean Cd concentration in the Fosu Lagoon sediment during the entire study is calculated as 0.78 ± 0.33 mg/kg. In a segment of Lake Huron (Ontario, Canada), where similar mean Cd concentration in sediment were observed (i.e., 0.77 mg/kg), lesser abundance of relatively sensitive taxa Ephemeroptera, Plecoptera, and Tricriptera occurred as compared to sites with lower Cd concentrations of 0.38 mg/kg.^[11]

Nickel. Figure 3 shows the sediment nickel levels for the different months at various sites in the Fosu lagoon. Significant site variations were observed (85.55% total variation; $P = < 0.0001$). Similar to Cd, the monthly variations in Ni concentrations were statistically insignificant (1.55% total variation; $P = 0.5435$); but unlike Cd, no regular patterns amongst sites were observed.

The general lack of monthly (or seasonal) variability of Ni at the various sites may reflect the locally high Ni enrichment resulting from direct, uncontrolled and irregular discharges of Ni loads into the lagoon throughout the year. The most erratic Ni data occurred at site S7 during the February investigation, where the highest Ni concentration was recorded (0.58 mg/kg). This suggests a temporarily Ni-related anthropogenic activity that might have occurred in February in the proximity of this site. Presumably, dilution with fresh sediment may have however reduced the concentration over the subsequent months (Fig. 3).

The general increasing trend for the average Ni levels over the eight-month survey period is as follows: S5 (0.15 ± 0.01) < S6 (0.186 ± 0.003) < S8 (0.25 ± 0.02) < S1 (0.26 ± 0.02) < S7 (0.30 ± 0.13) < S3 (0.43 ± 0.02) \cong S4 (0.43 ± 0.03) < S2 (0.47 ± 0.02). As in the case of Cd, site S2 representing the anthropogenic source of contamination by automobile repair and related activities (e.g., the careless disposal of overused nickel hydride and nickel-cadmium batteries) is the most Ni contaminated site in the lagoon. On the other hand, activities from S5 that seem to contribute significant load of Cd to the lagoon, is the least contributor of Ni to the Fosu Lagoon sediment. Sites S3 and S4, which recorded comparable Ni concentrations to S2, are both at the eastern sector of the lagoon.

The Canadian ISQG marine or freshwater sediments guidelines for Ni have not been established, but LEL guideline by OMOEE in freshwater sediment is 16 mg/kg. The mean Ni concentration in the Fosu Lagoon sediment during the entire study is calculated as 0.31 ± 0.12 mg/kg. The Ni concentrations in the Fosu Lagoon sediments are by far lower than this guideline and are also lower than in some reported sediments from some other African Atlantic estuaries (e.g., in Morrocco (49–135 mg/kg);^[24]).

Zinc. As shown in Figure 4, there was no regular trend and not much monthly variation in the sediment Zn concentration (0.20% total variation; P

= 0.0652), although site variations in this metal were very significant (99.16% total variation; $P < 0.0001$). The increasing trend for the mean Zn levels at the various sites is as follows: S6 (0.32 ± 0.05) < S1 (0.35 ± 0.02) < S5 (0.43 ± 0.02) < S3 (0.73 ± 0.04) < S8 (0.75 ± 0.02) < S4 (1.00 ± 0.02) \cong S2 (1.01 ± 0.04) < S7 (1.15 ± 0.02). Site S7, which recorded the highest Zn in the sediment of the Fosu Lagoon, is the point site behind a recreational area for a secondary school and where the laboratory waste from this institution is discharged directly without treatment to the lagoon. This supports the conclusion from an earlier investigation that the input of Zn into the lagoon sediment is largely from the school laboratories.^[18] Sites S2 (area of cluster of mechanical workshops) and S4 (automobile municipal garage and workshop) both at the eastern sector of the lagoon receive similar loads of automobile related wastes and recorded similar Zn in their sediments. Sites S8 and S3 being close to the sites with the highest Zn load also recorded relatively higher Zn concentrations in the sediment.

Zinc is an essential trace element that can be toxic to aquatic biota at elevated concentrations in the sediment of an aquatic system. The Canadian interim zinc marine/estuarine sediment guideline for the protection of aquatic lives is 124 mg/kg and all the Zn data collected during the survey period were two orders of magnitude lower than this guideline.

Manganese. As in the case of the other studied metals, the variations in the monthly sediment Mn concentration at the various sites were not large as compared to site variations in the metal concentration (Fig. 5). Nevertheless, differences in the monthly data for the eight sites studied were generally greater for Mn, which showed an average coefficient of variation (CV) of 21.4% as compared to 10.9%, 10.0%, 5.3% and 5.0% for Ni, Cd, Fe and Zn respectively. The sites that experienced most monthly variations in Mn concentrations were sites S4 (CV = 106.4%), S2 (CV = 21.2%) and S7 (13.8%). Similar monthly trends were observed for sites S5 and S7 ($R^2 = 0.92$) both of which are points of entry of garbage into the lagoon and serve as fishing grounds, where practices such as leaving cut branches of trees in the lagoon for fishing purposes are common.

As shown in Figure 5, the main anthropogenic contribution of Mn to the lagoon sediment originate from sampling site S1. This site that recorded a mean Mn concentration of 2.66 ± 0.24 mg/kg is at the northern side of the lagoon and is one of the highly populated parts of Cape Coast (Adisadel Estate). All effluents from homes enter the lagoon at several points in the area. The human activity is so much that eutrophication has caused sedimentation and one can walk many meters on waterweeds through the lagoon. In fact, part of the lagoon at this point has become a dumping site for domestic waste and sewage. Despite the relatively high Mn contamination in the sediment at this site, the concentration level is still far lower than the

OMOEE LEL bed sediment guideline of 457 mg/kg for the protection of aquatic lives.

The decreasing trend for the mean Mn levels for the remaining sites is as follows: S2 (0.81 ± 0.17) > S8 (0.76 ± 0.02) > S6 (0.725 ± 0.004) > S7 (0.61 ± 0.08) > S5 (0.50 ± 0.05) > S3 (0.35 ± 0.03) > S4 (0.17 ± 0.19). Although S2, the industrial activity related site, recorded the second highest sediment Mn concentration, the likely origin seems to be the litter and load of garbage disposed by the workers and clients of the busy mechanical shops. The same is applicable to sites S8, S7 and S6, which receive either domestic wastes, and litter from nearby settlements, institutions and recreation sites.

Iron. Fe was the most abundant metal measured and its variations amongst sites though statistically different (1.55% total variation; $P = 0.5435$) were relatively not much as compared to the other surveyed heavy metals (Compare Fig. 6 to Figs. 2 to 5). Likewise, apart from Zn, monthly variations in heavy metal concentration were least for Fe (see Fig. 6), suggesting this metal to be the most conserved amongst the studied metals in the Fosu lagoon sediment. The mean Fe concentrations in sediments at the various sites fall within a limited range of 0.36 g/kg (S7) to 0.39 g/kg (S2 or S6). These values are still lower than OMOEE LEL sediment Fe guideline of 21.2 g/kg, as well as some reported 16.0–40.3 g/kg sediment Fe concentration for some other Atlantic estuaries in Morocco.^[24]

Enrichment Factor Calculations as Evidence of Anthropogenic Origin of the Heavy Metals

Metal loads from natural and anthropogenic sources accumulate together, therefore, in order to differentiate the fraction of the element concentration originating from natural sedimentary sources from the anthropogenic fraction, normalizing tools are needed.^[25] To reduce the heavy metal variability caused by grain size and mineralogy of the sediments, and to identify anomalous metal contributions, geochemical normalization has been used with various degrees of success by employing various conservative metals including Fe.^[26] The heavy metal concentrations in the Fosu lagoon sediments are being normalized using Fe as a conservative element to evaluate anthropogenic sources of the metals. The conservativeness of Fe in bed sediments has received confirmation in this study for the Fosu Lagoon (see previously), despite the possible anthropogenic contributions to the lagoon.

The enrichment factor (EF), which is the index of contamination formula for the sediment samples, was calculated using the heavy metal average concentrations at sites S1 to S6 and S8 (target sites) and with the site S8 as baseline levels (Eq. 1). Site S8 is expected to receive the least anthropogenic metal load to the lagoon; being remote from the industrial activities, not a recreational center, and the least populated and apparently most environmentally

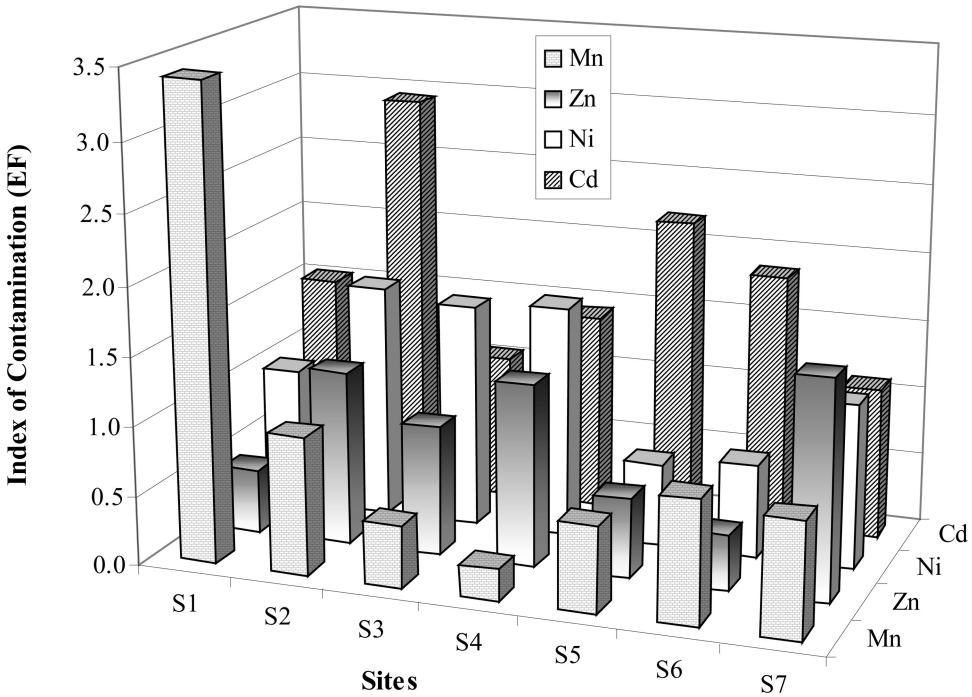


Figure 7: Index of contamination (EF) for Mn, Zn, Ni, Cd in the sediment at various suspected anthropogenic sites in the Fosu Lagoon as normalized to Fe and referenced to a relatively less contaminated site (S8).

educated settlements in the vicinity of the lagoon.

$$EF = \frac{\left(\frac{[M]}{[Fe]}\right)_{\text{target-site}}}{\left(\frac{[M]}{[Fe]}\right)_{\text{baseline}}} \tag{1}$$

where [M] is the metal studied.

The calculated EF values of the studied heavy metals as normalized to Fe for the various anthropogenic suspected sites is shown in Figure 7. Even though the calculated EF (especially for Zn) could be underestimated values (since the selected reference S8 also appears to be somewhat impacted by human activities), the values allowed us to identify places where anthropogenic inputs of particular metals were discharged (i.e., $EF > 1$).

The industrial activities at the eastern sector of the lagoon, especially the cluster of mechanical at Siwidu is the main source of Ni and Cd to the lagoon; although effluents from the hospital, refuse dumps and domestic effluents from Adisadel Housing Estates and a vague source from the southern segment all contribute anthropogenic loads of Cd into the lagoon. Anthropogenic Zn

Table 2: Correlation coefficients between the 7 studied sites in terms of their mean heavy metal (i.e., Cd, Ni, Zn, Mn and Fe) concentrations in the Sediments.

| | S1 | S2 | S3 | S4 | S5 | S6 | S7 |
|----|------|------|------|-------------|-------------|-------------|-------------|
| S1 | 1.00 | 0.21 | 0.21 | 0.36 | 0.02 | 0.30 | 0.00 |
| S2 | | 1.00 | 0.22 | 0.27 | 0.80 | 0.54 | 0.18 |
| S3 | | | 1.00 | 0.95 | 0.04 | 0.02 | 0.71 |
| S4 | | | | 1.00 | 0.07 | 0.02 | 0.51 |
| S5 | | | | | 1.00 | 0.79 | 0.01 |
| S6 | | | | | | 1.00 | 0.00 |
| S7 | | | | | | | 1.00 |

inputs also come from the industrial activities, but the major source of human activity related Zn input to the lagoon, is from the secondary school besides the lagoon. As mentioned earlier, laboratory effluents are discharged untreated into the lagoon. The main Mn input to the lagoon comes from domestic waste discharges from the highly populated residential area in the northern side of the lagoon.

Apart from Zn/Ni and Cd/Fe (both with $R^2 = 0.47$), the metal-metal correlations were generally very low with typical $R^2 \leq 0.22$. The poor correlation between the studied metals suggests that the heavy metals are independent of each other in terms of their origins. Although Zn and Ni or Fe and cadmium may have similar origins, it appears the correlation is obscured by the complexity of the multiple anthropogenic activities at the various sites.

Intersite Correlations

In order to find interrelations among sites in terms of their heavy metal input to the lagoon, correlation analyses between the sites' mean heavy metal (i.e., Cd, Ni, Zn, Mn and Fe) concentrations were calculated and the results are summarized in Table 2. Site S1 appears to be unique in terms of its heavy metal input into the lagoon, with the highest correlation coefficient of 0.36 (i.e., with S4). It is however noteworthy, that apart from the consistently high and invariant monthly Cd input from the hospital (S6)—see Figure 2, S1 correlates fairly well with S6 ($R^2 = 0.88$). Therefore, apart from the heavy metal discharge from the hospital institution-S6 characteristic of the residential area-S6 (i.e., domestic waste), the hospital could also be adding a constant source of Cd all year-round into the lagoon, perhaps from the laboratory or the general medical practices.

The $R^2 = 0.8$ for S2/S5 seems to suggest some interrelationships between the mechanical shop activities at Siwdu and the southern sector. As noted before, there are also some few mechanical/automobile activities in the southern part of the lagoon and although there is no evidence of a direct waste discharge

from these workshops to the lagoon as at Siwdu, run-offs from these workshops during heavy rains may also contribute heavy metals to this southern part of the lagoon.

The excellent correlation between S3/S4 ($R^2 = 0.95$) and the fairly good correlation between S5/S6 is expected in each case, because of the proximity of the pairs to similar anthropogenic activities in the area. Although S3 and S7 are not adjacent to each other, both sites are in areas for public recreational activities and appear to offer similar heavy input into the lagoon.

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

PAH Levels and Composition

Figure 8 shows the mean concentrations of the 15 individual PAH compounds identified in the sediment samples collected from 8 sites in the Fosu lagoon for the survey period in December 2003 and January 2004. The difference between the two sets of survey data was statistically insignificant ($P = 0.0666$). In terms of the individual compounds, the least abundant PAH compounds in the lagoon sediment were the compounds of molecular weights 166–202 (i.e., fluorene, carbazole, phenanthrene, anthracene, fluoranthene, and pyrene), followed by the two isomeric compounds benzo[a]anthracene and chrysene with molecular weights 228. The highest PAHs were recorded by compounds with molecular weights ranging from 128–154 (i.e., naphthalene, acenaphthalene and acenaphthene) and those from 252–276 (i.e., benzo[a]fluoranthene, perylene, benzo[a]pyrene, and benzo[g,h,i] perylene). As can also be observed from the standard deviations in Figure 8, there were huge variations between sites for some compounds (e.g., acenaphthene, acenaphthylene and benzo[a]pyrene), whereas the concentrations of the majority of compounds were comparable at the various sites.

As far as the compositional pattern of PAHs is concern, the lagoon was generally dominated with three- and five-ring compounds and in decreasing order by four-ring, six-ring and two-ring PAH compounds (Fig. 9). Only naphthelene and benzo[g,h,i] perylene were identified as the two-ring and six-ring members, respectively, present in the lagoon.

Table 3 shows the detailed data of PAH levels at the various sites. The concentrations of total PAHs in the sediment samples ranged from 254 mg/kg (S7 in December 2003) to 558 mg/kg (S2 in January 2004), with a mean concentration of 359.4 mg/kg. These levels of sediment contamination at the Fosu Lagoon are high as compared to many aquatic sites in the world. Zhou and Maskaoui have summarized the total PAH concentrations in sediments from various aquatic sites in the world,^[27] and the observed mean PAH in the Fosu lagoon is higher than 66.7 mg/kg, which is the highest mean PAH in

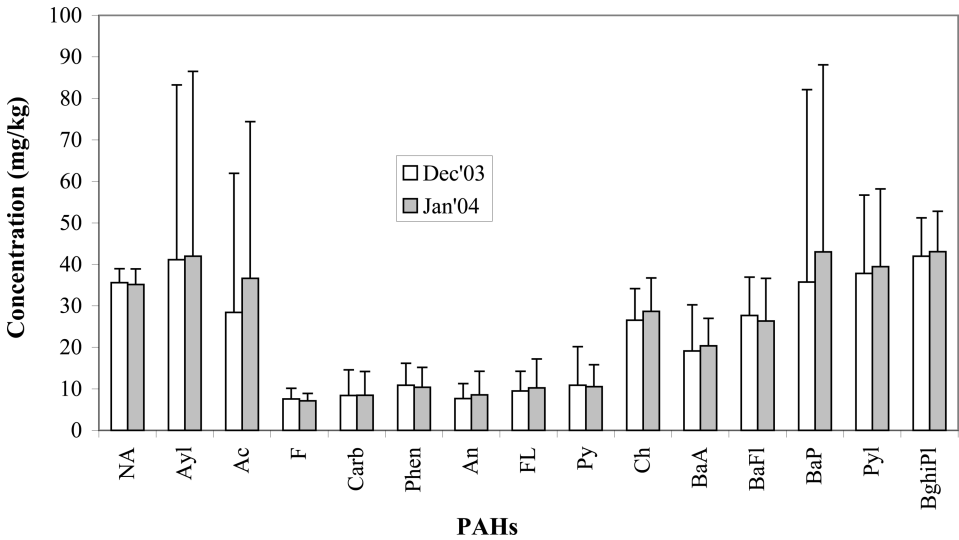


Figure 8: Mean concentrations of PAHs in sediment samples of the Fosu Lagoon

their report. This was reported for Kitimat Harbour in Canada.^[28] There were however, larger variations in the Kitimat Harbour samples and some higher PAH concentrations (e.g., 528 mg/kg as the highest) were recorded at some localized sites in the Kitimat Harbour. All the other reported locations by Zhou and Maskaoui, however, recorded PAH concentrations at least, one order of magnitude lower than those measured in the Fosu lagoon.

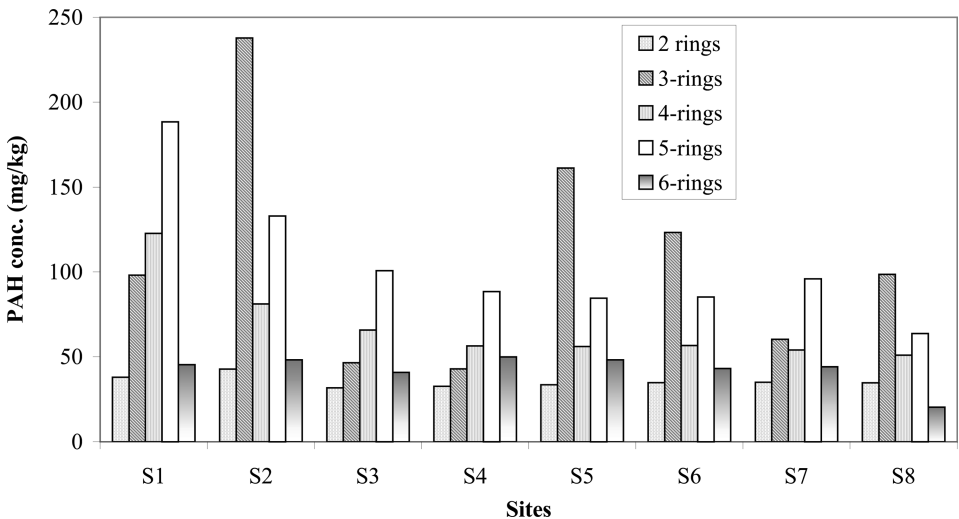


Figure 9: Concentration and composition pattern of PAHs in sediments of the Fosu Lagoon.

Table 3: PAH levels in the Fosu Lagoon.

| Compounds | Concentration (mg/kg) | | | | | | | | | | | | | | | |
|-----------------------|-----------------------|-------|------|------|------|------|------|------|--------------|-------|------|------|------|------|------|------|
| | December 2003 | | | | | | | | January 2004 | | | | | | | |
| | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 |
| Naphthalene | 37.9 | 42.9 | 32.8 | 33.4 | 33.4 | 35.0 | 34.2 | 35.1 | 38.0 | 42.6 | 30.7 | 31.7 | 33.7 | 34.5 | 35.8 | 34.1 |
| Acenaphthylene | 9.9 | 90.3 | 6.0 | 9.2 | 92.0 | 93.0 | 9.9 | 18.9 | 10.1 | 100.1 | 4.8 | 4.7 | 92.6 | 93.5 | 9.8 | 20.1 |
| Acenaphthene | 14.4 | 101.2 | 12.0 | 4.2 | 43.5 | 5.0 | 4.9 | 42.1 | 15.2 | 121.1 | 11.5 | 11.5 | 43.2 | 5.0 | 43.5 | 42.0 |
| Fluorene | 8.9 | 8.4 | 12.4 | 5.2 | 6.2 | 5.3 | 5.3 | 8.9 | 9.8 | 8.8 | 6.2 | 6.3 | 6.2 | 5.3 | 5.5 | 8.9 |
| Carbazole | 23.0 | 3.6 | 6.0 | 7.9 | 4.3 | 6.2 | 7.0 | 9.2 | 21.9 | 4.3 | 7.7 | 7.7 | 5.0 | 6.2 | 5.1 | 9.9 |
| Phenanthrene | 23.4 | 12.9 | 7.5 | 8.6 | 8.3 | 8.4 | 8.5 | 9.3 | 21.2 | 12.9 | 6.3 | 7.8 | 8.0 | 8.5 | 8.9 | 9.5 |
| Anthracene | 16.0 | 6.0 | 6.1 | 6.3 | 6.9 | 5.1 | 5.2 | 9.5 | 22.4 | 6.1 | 6.5 | 6.3 | 6.3 | 5.1 | 6.9 | 8.9 |
| Fluoranthene | 16.9 | 17.0 | 6.3 | 6.2 | 8.2 | 6.3 | 6.3 | 8.9 | 24.1 | 17.3 | 5.4 | 6.3 | 6.4 | 6.3 | 4.8 | 11.1 |
| Pyrene | 32.1 | 16.1 | 5.4 | 5.5 | 6.9 | 6.1 | 6.4 | 8.7 | 16.1 | 16.0 | 18.1 | 5.5 | 5.5 | 7.1 | 7.3 | 8.8 |
| Chrysene | 32.0 | 34.0 | 28.1 | 25.0 | 23.4 | 30.1 | 30.0 | 9.7 | 46.1 | 33.7 | 21.6 | 28.2 | 25.6 | 28.1 | 23.1 | 23.1 |
| Benzo(a)-anthracene | 46.0 | 14.2 | 18.2 | 17.9 | 17.3 | 14.3 | 14.6 | 10.4 | 32.2 | 13.9 | 28.3 | 18.1 | 18.9 | 15.0 | 15.5 | 21.2 |
| Benzo(a)-fluoranthene | 38.1 | 46.2 | 22.1 | 22.1 | 22.1 | 24.4 | 24.4 | 21.9 | 38.2 | 46.2 | 16.3 | 22.5 | 22.8 | 23.5 | 21.5 | 19.6 |
| Benzo(a)-Pyrene | 150.0 | 28.8 | 16.3 | 16.3 | 16.0 | 18.3 | 18.2 | 22.2 | 150.3 | 28.2 | 49.1 | 16.7 | 17.0 | 19.1 | 43.6 | 20.1 |
| Perylene | 0.20 | 58.3 | 49.1 | 50.1 | 41.1 | 42.1 | 42.1 | 19.4 | 0.03 | 58.3 | 48.5 | 49.1 | 50.2 | 43.0 | 42.2 | 24.1 |
| Benzo(g,h,i)-perylene | 44.8 | 48.2 | 41.5 | 49.8 | 45.1 | 43.0 | 43.2 | 20.1 | 45.8 | 48.3 | 40.1 | 50.1 | 51.3 | 43.2 | 45.0 | 20.8 |
| Σ (PAHs) | 494 | 528 | 270 | 268 | 375 | 343 | 260 | 254 | 491 | 558 | 301 | 273 | 393 | 343 | 319 | 282 |

Spatial Distribution

The highest concentration was observed at site S2 followed by S1. The least concentration, as expected, was at site S8. Since the samples were all collected at site points close to where refuse and other effluents are discharged, it seems the PAH load may principally originate from these sources. Variations in the quantity and type of the individual PAH compounds at the various sites would then reflect the main activities in these areas and the associated type and nature of refuse/effluents discharged at these points into the lagoon. More detailed source assessment of the PAH compounds in terms of the petrogenic or pyrolytic origins is discussed next. Some general comments with regards to the possible locations and the general anthropogenic activity in the area responsible for the varying distribution of PAH compounds in the sediment of the Fosu Lagoon are being made here.

The magnitude of total PAH from sites S2 and S1 reflects the heavy load of refuse/effluent discharge, respectively, from the automobile repair/spraying activities in the northeastern part of the lagoon and from domestic sources in the highly populated residential area at the northern sector of the lagoon. Though both sites recorded high concentrations of PAHs, there was a difference in the compositional pattern. Whereas five-ring compounds dominated at S1, the three-ring compounds dominated at S2 (Fig. 8). This distinguishes the source of PAH loads to these sites.

Sample S5 collected from the southern part of the lagoon ranked third in the PAH contamination. Although the southern segment of the lagoon is not as populated as the northern sector or has no major industrial activities as in the northeast, this is the smallest part of the lagoon and hence relatively smaller pollutants tend to concentrate in the small area. Incinerated household refuse, effluents and sewage discharge, unbent petroleum products from two nearby filling stations, and vehicular emissions from the heavily trafficked bridge in the southern sector are all potential sources of PAHs, with the sediment as an ultimate sink. Being a "closed lagoon," fresh input from the sea to dilute such inland-based pollutants is also minimal. The sediment sample associated to the hospital (S6) was the fourth highest sample in PAH concentration and this may likely reflect sewage discharged from the hospital area into the lagoon.

Although comparable levels of the different PAH compounds were generally found for most sites, some compounds were more predominant at some specific sites. For example, carbazole, phenanthrene and anthracene (3 rings), benzo[a]anthracene (4 rings) and particularly benzo[a]pyrene (5 rings) were more abundant at site S1. Acenaphthylene and acenaphthene (3 rings) were more characteristic at sites S2 and S5; even though S6 showed comparable levels of acenaphthylene as S2 and S5, the acenaphthene level was substantially different. Also, the fluoranthene levels were higher at S1 or S2 than the other sites, being approximately 2 to 4 times greater.

Source Assessments

The differences in the type of PAH compounds at the different sites indicate that there are potentially different sources of PAHs in the area; possibly including sewage outfalls, industrial wastewater, thermal combustion processes (e.g., cooking and heating oils, and coal burning) followed by atmospheric fallout, oil residues, vehicular emissions (e.g., automobiles and trucks), and biomass burning (e.g., fire woods, charcoal, etc).^[29,30] From inspection of the distribution of PAHs in the surface sediments alone, it is often difficult to differentiate between the sources of inputs. The distribution of alkylated PAHs to parent PAH is one means of characterizing PAH sources,^[31] however, logistic reasons did not permit the measurement of the alkylated PAHs in this present study. The ratios of specific parent PAH compounds have also been identified to be one approach to distinguish between different sources of PAH in a particular environmental matrix,^[32,33] and this method is used in the present study to characterize the PAH sources to the lagoon. Correlation analyses can also provide information about associations between sites, between the individual PAH compounds, and between some specific PAH compounds and heavy metals to determine common origins.

Site Correlations

Correlation analyses between the sites' individual PAH compound levels ($n = 15$) indicates no significant correlation between S1 and any other site, suggesting the unique origin of PAHs from this site. As observed also for Cd, S2 correlates best with S5 ($R^2 = 0.72$) in terms of the PAH levels. The correlation between the two sites for the individual PAH compounds is also reflected in the similarities of the compositional patterns at these two sites (Fig. 9). Sites S3, S4 and S7 interrelates well with each other in terms of their PAH levels; S3/S4 ($R^2 = 0.87$), S3/S7 ($R^2 = 0.87$) and S4/S7 ($R^2 = 0.83$); also see Figure 9. This relationship was also observed with the heavy metals and may relate to the fact that S3 and S7 are both in the vicinity of recreational grounds and also that these 3 sites essentially form an "equilateral triangle" across the lagoon (i.e., they are of approximately equal distance from each other). S5 and S6 being close to each other also show good correlation ($R^2 = 0.83$). However, despite the closeness of S7 to S8, their correlation is only fair ($R^2 = 0.41$), suggesting that PAH origins from these sites are quite different to overcome the site proximity.

PAH Interrelationships

In order to assess PAH associations and their possible origins, correlation analyses were conducted among the concentration of the individual PAHs in

the surface sediments. The results are summarized in Table 4. It is known that where two compounds have a common source, there is more likely to be a correlation between their concentrations.^[34]

Close relationships were found between individual PAH compounds. Carbazole, anthracene, phenanthrene and benzo[a]pyrene show the highest PAH-PAH inter-relations with correlation coefficients of $R^2 = 0.81 \pm 0.06$ with each other. The results reveal that these compounds, and to a lesser extent pyrene, were possibly derived from a common anthropogenic origin. One of these compounds, carbazole-being a nitrogen-containing heterocyclic aromatic hydrocarbon, is usually found in coal tar- and oil- contaminated environments as a product of incomplete combustion.^[35] There seems to be another origin for carbazole and benzo[a]pyrene, which is exclusive to benzo[a]anthracene (BaA/BaP (0.75), BaA/Carb (0.73) and BaP/Carb (0.85)). This other source is independent of phenanthrene, since essentially no correlation was found between benzo[a]anthracene and phenanthrene ($R^2 = 0.01$). Some other close relationships between individual PAH compounds included Fl/Phen (0.75) and Fl/BaFl (0.72), although phenanthrene and benzo[a]fluoranthene correlations were weak.

Apart from chrysene, with which benzo[g,h,i]perylene (6 fused aromatic rings) seems to demonstrate some modest correlation ($R^2 = 0.33$), this latter compound shows no significant correlation with any of the other PAH compounds measured. It is noteworthy that apart from site S8, there were not significant variations in the concentration of this compound at all other sites (i.e., 45.7 ± 3.3 mg/kg). In almost all cases, perylene (containing 5 fused aromatic rings) showed inverse correlation with the other PAH compounds; being strongest with carbazole (0.82), phenanthrene (0.77), anthracene (0.77) (all containing 3 fused aromatic rings). It is possible that some fraction of these compounds is from the biodegradation of perylene by natural occurring population of sediment microorganisms. We intend to embark on another project, which would focus on evaluating the degradation capability of the indigenous microflora in this PAH-contaminated lagoon sediment and the development of clean up bioremediation technologies by natural attenuation.^[36] Preliminary investigation of the microbial population densities in the lagoon water shows an uncountable number of bacteria populations.^[37]

PAH Heavy Metal Interrelationships

No statistically significant correlation was found between Ni, Fe, and Zn with any of the measured PAH compounds. There was however, a negative correlation between Mn and perylene ($R^2 = 0.71$, $P = 0.0045$) and significant positive correlations between Mn and 8 of the PAH compounds as follows. Phen ($R^2 = 0.93$, $P < 0.0001$), BaP ($R^2 = 0.92$, $P < 0.0001$), An ($R^2 = 0.88$, $P = 0.0003$), Carb ($R^2 = 0.81$, $P = 0.0011$), Py ($R^2 = 0.75$, $P = 0.0027$), Fl

Table 4: Correlation coefficients for PAH compounds in the sediments at different eight locations and for two survey periods (n = 16).

| | NA | Ayl | Ac | F | Carb | Phen | An | Fl | Py | Ch | BaA | BaFl | BaP | PyI | BghiPl |
|--------|------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|--------|
| NA | 1.00 | 0.17 | 0.58 | 0.10 | 0.01 | 0.36 | 0.06 | 0.60 | 0.24 | 0.25 | 0.00 | 0.89 | 0.10 | 0.03 | 0.00 |
| Ayl | 0.17 | 1.00 | 0.26 | 0.05 | 0.23 | 0.13 | 0.13 | 0.01 | 0.01 | 0.02 | 0.15 | 0.11 | 0.11 | 0.07 | 0.17 |
| Ac | 0.58 | 0.26 | 1.00 | 0.07 | 0.12 | 0.01 | 0.02 | 0.19 | 0.04 | 0.01 | 0.09 | 0.40 | 0.02 | 0.00 | 0.10 |
| F | 0.10 | 0.05 | 0.07 | 1.00 | 0.13 | 0.18 | 0.21 | 0.30 | 0.11 | 0.05 | 0.07 | 0.14 | 0.11 | 0.09 | 0.12 |
| Carb | 0.01 | 0.23 | 0.12 | 0.13 | 1.00 | 0.72 | 0.85 | 0.37 | 0.44 | 0.17 | 0.73 | 0.07 | 0.85 | 0.01 | 0.82* |
| Phen | 0.36 | 0.13 | 0.01 | 0.18 | 0.72 | 1.00 | 0.73 | 0.75 | 0.63 | 0.39 | 0.01 | 0.14 | 0.84 | 0.01 | 0.77* |
| An | 0.06 | 0.13 | 0.02 | 0.21 | 0.85 | 0.73 | 1.00 | 0.57 | 0.33 | 0.23 | 0.52 | 0.14 | 0.84 | 0.01 | 0.77* |
| Fl | 0.60 | 0.01 | 0.19 | 0.30 | 0.37 | 0.75 | 0.57 | 1.00 | 0.43 | 0.46 | 0.21 | 0.72 | 0.50 | 0.00 | 0.26* |
| Py | 0.24 | 0.01 | 0.04 | 0.11 | 0.44 | 0.63 | 0.33 | 0.43 | 1.00 | 0.12 | 0.62 | 0.36 | 0.62 | 0.00 | 0.24* |
| Ch | 0.25 | 0.02 | 0.01 | 0.05 | 0.17 | 0.39 | 0.23 | 0.46 | 0.12 | 1.00 | 0.15 | 0.45 | 0.30 | 0.33 | 0.03* |
| BaA | 0.00 | 0.15 | 0.09 | 0.07 | 0.73 | 0.01 | 0.52 | 0.21 | 0.62 | 0.15 | 1.00 | 0.04 | 0.75 | 0.01 | 0.44* |
| BaFl | 0.89 | 0.11 | 0.40 | 0.14 | 0.07 | 0.14 | 0.14 | 0.72 | 0.36 | 0.45 | 0.04 | 1.00 | 0.21 | 0.12 | 0.01* |
| BaP | 0.10 | 0.11 | 0.02 | 0.11 | 0.85 | 0.84 | 0.84 | 0.50 | 0.62 | 0.30 | 0.75 | 0.21 | 1.00 | 0.01 | 0.62* |
| PyI | 0.03 | 0.07 | 0.00 | 0.09 | 0.01 | 0.01 | 0.01 | 0.00 | 0.00 | 0.33 | 0.01 | 0.12 | 0.01 | 1.00 | 0.16 |
| BghiPl | 0.00 | 0.17 | 0.10 | 0.12 | 0.82* | 0.77* | 0.77* | 0.26* | 0.24* | 0.03* | 0.44* | 0.01* | 0.62* | 0.16 | 1.00 |

Compound abbreviations: naphthalene (NA), acenaphthylene (Ayl), acenaphthene (Ac), Fluorene (F), carbazole (Carb), phenanthrene (Phen), anthracene (An), fluoranthene (Fl), pyrene (Py), chrysene (Ch), benzo(a)anthracene (BaA), benzo(a)fluoranthene (BaFl), benzo(a)pyrene (BaP), perylene (PyI), benzo(ghi)perylene (BghiPl). *implies a negative correlation.

($R^2 = 0.68$, $P = 0.0058$) and Ch ($R^2 = 0.46$, $P = 0.0317$). Many trees and shrubs are capable of taking up adequate amount of Mn and it is therefore possible that Mn and the associated PAH compounds in the sediments, at particularly S1, originate from combustion of domestic materials including woods and shrubs. This possibility is further discussed below using ratios of PAH as source indicators.

Cd also showed statistically significant correlation with four PAH compounds, namely Ayl ($R^2 = 0.72$, $P = 0.008$), Ac ($R^2 = 0.53$, $P = 0.0199$), BaFl ($R^2 = 0.52$, $P = 0.0222$) and NA ($R^2 = 0.51$, $P = 0.0230$). High levels of these compounds are also characteristic of site S2, suggesting that the industrial activities from the nearby mechanical shop may be responsible for the higher input of these chemicals to the Fosu lagoon.

PAH Isomer Pair Ratios as Diagnostic Source Indicators

The ratios of specific PAH compounds have been identified to possess the potential to distinguish natural and anthropogenic sources.^[32,33] To minimize confounding factors such as differences in volatility, water solubility, adsorption etc. ratio calculations are usually restricted to PAHs within a given molecular mass.^[33] Combustion and/or anthropogenic input is often inferred from an increase in the proportion of the less stable PAH isomer relative to the more stable isomer. Yunker et al.^[33] have summarized the literature on PAH ratios for petroleum, single-source combustion and some environmental samples and made the following conclusions. For mass 178, an anthracene to anthracene plus phenanthrene ($An/\{An+Phen\}$) ratio <0.10 usually is an indication of petroleum while a ratio >0.10 indicates dominance of combustion. For mass 202, a fluoranthene to fluoranthene plus pyrene ($Fl/\{Fl+Py\}$) ratio of 0.40 seems to be the petroleum/combustion transition point, though not definite. Ratios between 0.40 and 0.50 are more characteristic of liquid fossil fuel (vehicle and crude oil) combustion whereas ratios >0.5 are characteristic of grass, wood or coal combustion. For mass 228, a benzo[a]anthracene to benzo[a]anthracene plus chrysene ratio <0.20 imply petroleum, 0.20 to 0.35 indicates either petroleum or combustion, and >0.35 imply combustion.

The ratios of the above-specified PAHs in the Fosu lagoon were calculated and are shown in Table 5. The $An/An+Phen$ ratios are all ≥ 0.1 , suggesting combustion sources of PAH from all eight sites. However, the smaller ratios obtained for S2 and to some extent S6 distinguishes them from the other sites. It appears there is mixed petroleum and combustion sources at these sites. The mixed petroleum and combustion sources at these two sites is confirmed from the $BaA/(BaA+Chr)$ fraction, where ratios of 0.29 (S1) and 0.34 (S6), which falls within the generally observed mixed-source ratio of 0.2–0.35 for mixed petroleum/ combustion origin of pollution are observed. The $BaA/(BaA+Chr)$

Table 5: PAH ratios of sediments from the Fosu Lagoon.

| Ratio | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | Source Patterns from the literature ^[32,33] |
|---------------|-------|------|------|------|------|------|------|------|--|
| An/(An+Phen) | 0.46 | 0.32 | 0.48 | 0.43 | 0.45 | 0.38 | 0.41 | 0.49 | >0.10: combustion source; <0.10: unburned petroleum source |
| Fl/(Fl+Py) | 0.47 | 0.52 | 0.38 | 0.53 | 0.54 | 0.49 | 0.45 | 0.53 | >0.50: biomass & coal combustion 0.4–0.5: petroleum combustion <0.40: unburned petroleum |
| BaA/(BaA+Chr) | 0.50 | 0.29 | 0.48 | 0.40 | 0.42 | 0.34 | 0.36 | .050 | >0.35: combustion 0.20–0.35: mixed petroleum/combustion <0.2: unburned petroleum source |
| BaP/(BghiPl) | 750.0 | 0.49 | 0.33 | 0.33 | 0.39 | 0.43 | 0.43 | 1.14 | 1.2–5.0: wood burning and coal burning ⁽³⁸⁾ |

Compound abbreviations in Table 3.

ratios of ≥ 0.35 re-echo the predominance of combustion as the main source of PAH from the remaining sites.

The Fl/Fl+Py ratios whose interpretations are said to be more definitive^[33] provided more distinctions between the sites. Based on 0.4 as the transition ratio, the calculated 0.38 suggests a petrogenic source for S3, mixed petroleum and combustion sources for S1, S6, and S7 and a predominance of combustion at S2, S4, S5, and S8. Despite the lack of consistency in some cases, there seems to be a general consensus by all the three ratio indicators that combustion is the dominant source of PAH input into the lagoon. Although not conclusive, there is also an indication of petrogenic source contributions to sites such as S2, S3 and S6. Future studies in the lagoon to include the measurement of alkylated PAHs may also be helpful in providing more conclusive source characterization of the PAHs to the lagoon.^[31]

Variations in additional input sources (e.g., high or medium temperature combustion processes, different fossil materials) may also account for the differences in the composition pattern of PAHs between sampling sites (Table 5 and Fig. 9).^[27] Despite the apparent dominance of combustion as the major source of anthropogenic PAH to the Fosu lagoon at most sites (using the ratio indicators above), the BaP/BghiPl ratios suggests wood and coal burning only for site S1 (Table 5). It is therefore possible that combustion of liquid fossil fuel is the major source of PAH to the lagoon at the other sites. As mentioned earlier, the high Mn levels support the possibility of wood (trees and shrubs)

origin at particularly S1. This is further supported by the strong correlations between Mn and the individual PAH compounds characteristic at this site.

Risk Assessment

Concern over PAHs for the study is associated with their known carcinogenic behavior. Due to their relatively low solubility in water and their hydrophobic nature, PAHs may accumulate to high concentrations in sediments.^[11,29,32] The Canadian Council of Ministers of the Environment (CCME)^[11] has, among other PAH compounds, set an interim marine/estuary or freshwater sediment guidelines for 11 out of the 15 analyzed PAH compounds for the protection of aquatic life exposed to bed sediments. Water column organisms have been experimentally observed to be at risk if site related sediments are above the probable effect level (PEL) guidelines.^[11] These values are therefore being used to evaluate the risk potential of aquatic lives in the Fosu lagoon. Even though the conditions of the Canadian waters may be different, in the absence of any such standard in Ghana, such evaluation would be very informative.

For each site, mean PEL quotients were calculated for PAHs by dividing the concentrations of the individual PAH compounds by their respective PEL guidelines, summing these quotients and dividing by the total number of PAHs (i.e., 11).^[32] The mean quotients accounted for the presence of mixtures of toxic chemicals and degree to which individual chemicals exceeded their guidelines. The method assumes additivity of toxic effect (no synergistic or antagonistic effects) and a mean PEL quotient ≥ 1 implied that, at least one compound exceeded the PEL, and therefore adverse impact may occur. The decreasing order of magnitude of the calculated PEL quotient for the 8 sites is as follows:

S2 (212.01) > S5 (133.23) > S6 (94.16) > S8 (83.03) > S1 (77.84) > S7 (56.28) > S3 (43.33) > S4 (35.79). All sediment samples had a mean PAH PEL quotient far greater than 1, indicating high potential to have adverse effect on sensitive species.

CONCLUSION

The results of this study generally demonstrate that there are high levels of PAHs and some heavy metals in the sediment of the Fosu Lagoon. Exceedances in Cd sediment concentrations to some established guidelines were recorded at some sites in the Fosu lagoon. All the sediment samples had a mean CCME PAH probable effect level (PEL) quotient far greater than 1, indicating high potential to have adverse effect on sensitive species. With the exception of iron, which appeared to be conserved, there was a significant variation in the sediment heavy metal and PAH concentrations between

the sampling sites. Monthly variations at individual sites were however lacking.

Good site correlations were observed for sediment samples from a mechanical shop in the eastern section of the lagoon and the southern sector of the lagoon in terms of the PAH and Cd levels. The two recreational ground sites (S3 and S7) and one other site in their vicinity seem to inter-relate in terms of both their PAH levels and heavy metal metals. Close relationships were also found between individual PAH compounds. Carbazole, anthracene, phenanthrene and benzo[a]pyrene showed the highest PAH-PAH associations. The results reveal that these compounds were possibly derived from a common anthropogenic origin. In almost all cases, perylene (containing 5 fused aromatic rings) showed inverse correlation with the other PAH compounds; being strongest with three compounds containing 3 fused aromatic rings. It is speculated that some fraction of these compounds could be from the biodegradation of perylene by natural occurring population of sediment microorganisms. Further studies are required to verify this speculation.

There seems to be a general consensus from some three PAH-PAH ratio indicators that combustion is the dominant source of PAH input into the lagoon. Although not conclusive, there is also an indication of petrogenic source contributions from some sites in the eastern segment, particularly in the vicinity of a mechanical/fitting shop.

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