Occurrence and Risk Assessment of Polycyclic Cyclic Aromatic Hydrocarbons (PAHs) and Their Nitrated Derivatives (NPAHs) at Nile River and Esmailia Canal in Egypt

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Abstract- Fresh water samples at three sites in Nile River (NR1, NR2 and NR3) and two sites in Esmailia canal (E1 and E2) in Egypt were collected. Concentrations of soluble and particulate phases of polycyclic aromatic hydrocarbons (PAHs) and nitrated derivatives (NPAHs) were determined by using HPLC with florescence detection and HPLC with chemilumnecence detection, respectively. The total average concentrations of the fifteen PAHs having two to six rings at NR1, NR2 and NR3 in summer and winter seasons were ranged from 2.47×10^3 to 3.20×10^3, 0.99×10^3 to 1.27×10^3 and 1.19×10^3 to 1.43×10^3 ng/l, respectively, while those at E1 and E2 were ranged from 6.17×10^3 to 7.55×10^3 and 1.27×10^4 to 1.73×10^4 ng/l, respectively. The concentrations of benzo[a]pyrene (BaP) at Nile River and Esmailia canal sites were varied from 26.4 to 83.2 ng/l. The total average concentrations of eight NPAHs having three to five rings at the same sites in summer and winter seasons were varied from 7.5 to 11.2, 5.2 to 7.0 and 5.7 to 8.0 ng/l at NR1, NR2 and NR3 respectively, and varied from 7.6 to 11.8 and 16.0 to 20.0 ng/l at E1 and E2 respectively. The major sources of PAHs and NPAHs in water environment were discussed based on the most widely used diagnostic ratios of PAH pairs and mono-NPAHs to their parent PAHs, indicating a mixed contamination sources with the predominance of petrogenic source origin at Nile River sites, and pyrogenic source origin at Esmailia canal sites in both summer and winter seasons.

BaP-equivalent carcinogenic power (BaPE) values for PAHs at Nile River and Esmailia canal sites in summer and winter seasons were varied from 19.9 to 81.3 ng/l, and from 87.7 to 378.9 ng BaPE /l, respectively. The indirect mutagenicity values calculated by PAH concentrations at Nile River and Esmailia canal sites in both seasons were varied from 26.4 to 83.2 and from 179.5 to 538.1 revertants/l, respectively. The direct mutagenicity at Nile River and Esmailia canal sites were varied from 14.0 to 25.9 and from 22.3 to 49.8 revertants/l, respectively in both seasons. The tendency that carcinogenicity and mutagenicity at Esmailia canal sites were much higher than those at Nile River sites was in accordance with the fact that Esmailia canal is more polluted with PAHs and NPAHs than Nile River.

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Index Terms- Polycyclic aromatic hydrocarbons, Nitrated Polycyclic aromatic hydrocarbons water pollution, Nile River, Esmailia canal.

1 INTRODUCTION

Water pollution by toxic organic compounds is a topic of worldwide concern. Polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs), hydrocarbons containing two or more fused benzene rings, are ubiquitous pollutants in the environment. Due to their ubiquitous occurrence, recalcitrance properties and suspected carcinogenicity and mutagenicity to humans and biota, PAHs are included in the priority lists of pollutants of the U.S. Environmental Protection Agency (EPA) and the European Union. The US EPA fixed 16 PAHs having two to six rings as priority pollutants, the latest being effective from 1997 [2], [22], [30], [36] some of PAHs and NPAHs are considered to be possible or probable human carcinogens. The endocrine disrupting properties of PAHs have been recently reported [31], [15], [5], [14]. The distribution in the environment and potential human health risks have thus become the focus of much attention.

Because of their hydrophobicity and low solubility, PAHs and NPAHs in the aquatic environment rabidly become associated with organic and inorganic suspended particles [11] and subsequent deposition in sediments. PAHs and NPAHs partition between truly dissolved, colloidal and particulate phases, which subsequently influences their mobility and availability in watersheds [19]. Because these contaminants have low water solubility, they are primarily associated to particles. Their mobility between phases depends not only on intrinsic physico-chemical properties of individual compounds (e.g., solubility, vapour pressure) [49] but also relies on environmental variables such as the amount of rainfall and morphological characteristics of drainage basins [24].

The introduction of wastewater effluent into drinking water aquifers and surface waters is becoming more common throughout the world [8].

PAHs emitted to the air can be transported over long distances before they are deposited with atmospheric precipitation on soils, vegetation or sea and inland waters [47], [41], [50]. The presence of PAHs and NPAHs in all these elements of the environment may create a risk not only to humans but to all living organisms.

Although some PAHs are naturally occurring, the majorities are anthropogenic and enter the environment through release of petroleum products (petrogenic sources) or by combustion of organic matter (pyrogenic sources) [34]. Recent studies have shown that pyrogenic sources predominate in

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urban settings and that the profile of PAHs in urban storm water resembles that of atmospheric deposition [7], [2], [23], [20]. However the NPAHs in the two phases have not been compared.

The discharge of PAHs from urban watersheds is exacerbated in arid regions. Arid urban watersheds have a tremendous number of sources. Moreover, the long antecedent periods without rain in arid regions potentially enhance the dry deposition of PAHs to urban landscapes from these atmospheric sources. When rainfall does occur, the precipitation is often short but intense. Runoff from these largely impervious urban surfaces efficiently mobilizes deposited material, including PAHs, in the resulting surface runoff [30], [35].

Water resources in Egypt are becoming scarce. Surface-water resources originating mainly from the Nile River are now fully exploited, while groundwater sources are being brought into full production. Egypt is facing increasing water needs, demanded by a rapidly growing population, increased urbanization, higher standards of living and an agricultural policy that emphasizes expanded production in order to feed the growing population. The population is currently increasing by more than one million people a year. One of the greatest water-related challenges facing Egypt is the pollution of its surface water resources from agricultural, domestic and industrial sources [25].

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In Egypt, there is a lack of published data on the distribution of certain contaminants such as PAHs and almost no published data about NPAHs in aquatic environment. The main purposes of this work are (i) to investigate the seasonal concentrations of PAHs and NPAHs in the Nile River and Esmailia canal, (ii) to determine the source origin of PAHs and NPAHs at the aquatic environment in Egypt, and (iii) to evaluate the risk assessment of such pollutants in the Egyptian fresh water environment.

These data gaps prompted the current investigation to evaluate the levels and distribution of PAHs in the Egyptian aquatic environment. Moreover, this is the first report to discuss the NPAHs in water system not only in Egypt but also in all African continent.

2 MATERIALS and METHODS

2.1 Chemicals

EPA610 PAH Mixture, containing naphthalene (Nap), acenaphthalene (Ace), fluorine (Fle), anthracene (Ant), phenanthrene (Phe), fluoranthene (Frt), pyrene (Pyr), benz[*a*]anthacene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a*,*h*]anthracene (DBA), benzo[*ghi*]perylene (BghiPe) and indo[*1*,*2*,*3-cd*]pyrene (IDP) were purchased as a PAH standard solution from Supleco (Bellefonte, PA, U.S.A). Five deuterated PAHs

(Nap-d_8, Ace-d_{10}, Phe-d_{10}, Pyr-d_{10} and BaP-d_{12}) were purchased from Wako Pure Chemical (Osaka, Japan) as internal standards and they were dissolved in acetonitrile (Kanto Chemical, Tokyo, Japan). While 1-nitropyrene (1-NP), 2-nitrofluorene (2-NF), 9-nitro- anthracene (9-NA), 3-nitroflourancene (3-NFR) and 2-fluoro-7-nitrofluorene (FNF, internal standard) were purchased from Aldrich Chemical (Milwaukee, WI, U.S.A.). 9-Nitrophenantherene (9-Nph) and 7-nitrobenz[*a*]anthracene (7-NBaA) were purchased from Accustandard Inc. (New Haven, CT, U.S.A). 6-Nitrobenzo[*a*]pyrene (6-NBaP) and 6-nitrochrysene (6-NC) were kindly provided by Dr. Nobuyuki Sera of Fukuoka Institute of Health and Environmental Science (Fukuoka, Japan). All other chemicals used were of analytical-reagent grade.

2.2 Sampling sites description

2.2.1 Nile River sampling sites

The Nile River is about 6,670 km (4,160 miles) in length and is the longest river in the world. Although it is generally associated with Egypt, only 22% of the Nile's course runs through Egypt. Three sites were selected to represent different sectors in Nile River (Fig. 1). The first site was Greater Cairo (NR1) at the intake of a drinking water treatment plant. At this location the electrical power station, ship maintenance center and Nile transportation discharged their wastewater into the River. This site is considered downstream of most Greater Cairo activities. The second site was Banha (NR2) (North Egypt) in the north part of Nile River at the beginning of delta area. This was a residential site affected mainly by agricultural waste loaded with different chemicals and toxic organic nutrients. The third site was Beni-Suif (NR3) (Upper Egypt) in the south part of River Nile. This site was affected by urbanization, traffic and some industries like cement and fertilizers facilities.

2.2.2 Esmailia canal sampling sites

Esmailia canal is 130 km long; it is a branch of Nile River which goes East to Greater Cairo to El-Sharquia governorate till Esmailia governorate in the Eastern part of Egypt. After that Esmailia canal is subdivided into two canals; Port-Said branch which goes to north to the Port-Said governorate and Suez branch which goes to the south to Suez governorate (Fig. 1).

Esmailia canal is one of the water sources for drinking and irrigation in North Greater Cairo and Suez canal area which includes Suez, Esmailia and Port-Said governorates. As well as it is the water source for El-Ameria and Mostorod in Greater Cairo and some parts in El-Sharquia governorate. Although Esmailia canal is a branch from Nile River in the north of Cairo, the quality of water is very different

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from the River Nile water. Esmailia canal water is very polluted especially in the first 10 km in Greater Cairo area due to presence of a lot of industries and oil companies.

Two sites were selected along the Esmailia canal, the first site (E1) located after 10 Km from the beginning of the canal so it was affected only by the urban activity and traffic emissions.

The other site (E2) located after 5 km from the beginning of the canal which affected by several kinds of pollutants come from different factories like paper, food, petroleum and petroleum derivatives industries that discharge their wastewater without treatment to Esmailia canal.

2.3 Sampling and extraction

Narrow neck glass bottles (previously washed with dichloromethane) were used to collect two liters surface water samples. Just after sampling, 100 ml (5%) of methanol were added to each sample. The solutions were filtered through a glass fiber filter paper (GC-50, 0.45 µm poor size) followed by using a 3M embore disc filtration (C18, 47 mm poor size). C18 discs were extracted using dichloromethane followed by super sonication twice, filtration through a glass filter paper, addition of 100 µm DMSO, evaporation followed by dissolving in 900 µl ethanol and then evaporation. Finally the sample solution was filtered through a membrane filter (HLC-DISK13). Other conditions were the same as in our previous paper [38], [39], [13], [26] [27]. In this study, the average concentrations of total PAHs and NPAHs were calculated from the eighteen grab water samples collected at three different sites (six samples from each site) in both seasons along the Nile River sites (NR1, NR2 and NR3) in summer and winter seasons (September, 2011 and February, 2012) . As well as twelve grab water samples were collected at two sites along Esmailia canal (E1 and E2) and also six samples at each site in both summer and winter seasons.

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2.4 Analysis

Fifteen PAHs were analyzed by using HPLC with fluorescence detection. The system consisted of two HPLC pumps (LC-10A, Shimadzu, Kyoto, Japan), a fluorescence detector (RF-10A, Shimadzu), a system controller (SCL-10A, Shimadzu), an integrator (Chromatopac C-R7Ae, Shimadzu), a degasser (DGU-14A, Shimadzu), an auto sample injector (SIL-10A, Shimadzu), a column oven (CTO-10AS, Shimadzu), a guard column (Inertsil ODS-P, 4.0 i.d. × 10 mm, GL Sciences Inc., Tokyo, Japan) and an analytical column (Inertsil ODS-P, 4.6 i.d. × 250 mm, GL Sciences Inc., Tokyo, Japan). The mobile

phase was a mixture of acetonitrile and water with a gradient concentration mode of acetonitrile. The flow rate was 1 ml/min. The time program of the fluorescence detector was set to detect at optimum excitation and emission wavelength for each PAH. NPAHs were analyzed by using HPLC with chemiluminescence detection with several modifications according to our laboratory detection method [37], [38].

The HPLC system consisted of two analytical columns (both Cosmosil 5C18-MS, 4.6 i.d. × 10 mm, Nacalai Tesque, Kyoto, Japan), two mobile phase pumps (LC-10A, Shimadzu, Kyoto, Japan), a chemiluminescence reagent solution pump (DMX-2000, Sanuki, Tokyo, Japan), a chemiluminescence detector (CLD-10A, Shimadzu, Kyoto, Japan), a system controller (SCL-10A, Shimadzu, Kyoto, Japan), a chromatopac integrator (C-R4A, Shimadzu, Kyoto, Japan), a degasser (DGU-14A, Shimadzu, Kyoto, Japan), an auto sample injector (SIL-10A, Shimadzu, Kyoto, Japan), a column oven (CTO-10AC, Shimadzu, Kyoto, Japan) and a guard column (Cosmosil 5C18-MS, 4.6 i.d. × 10 mm, Nacalai Tesque, Kyoto, Japan). The mobile phase was imidazole–perchloric acid buffer (pH 7.6)–acetonitrile (1:1) at a flow rate of 1.5 ml/min. The post-column chemiluminescence reagent solution was an acetonitrile solution containing 0.04 mM bis(2,4,6-trichlorophenyl) oxalate and 15 mM hydrogen peroxide at a flow rate of 1.0 ml/ min.

The validity of this method were already confirmed through our previous published reports showing the recoveries varied from 87 to 104%, limits of detection (S/N = 3) varied from 0.25 to 1.5 x 10^{-15} mol, and limits of quantification (S/N = 10) varied from 10^{-15} to 10^{-12} mol (over two orders) and showed a good linearity ($r^2 \geq 0.899$) [38], [13].

3 RESULTS

In this study, the seasonal concentrations of PAHs and NPAHs at Nile River and Esmaila canal sites were determined . The total average concentrations of the fifteen PAHs in NR1, NR2 and NR3 in summer and winter seasons were ranged from 2.47 × 10^3 to 3.20 × 10^3, 0.99 × 10^3 to 1.27 × 10^3 and 1.19 × 10^3 to 1.43 × 10^3 ng/l , respectively, while those for E1 and E2 were ranged from 6.17 × 10^3 to 7.55 × 10^3 and 1.27 × 10^4 to 1.73 × 10^4 ng/l, respectively. And the total average concentrations of the seven selected NPAHs at the designated sites in summer and winter seasons were varied from 7.5 to 11.2, 5.2 to 7.0 and 5.7 to 8.0 ng/l at NR1, NR2 and NR3, respectively, and varied from 7.6 to 11.8 and 16.0 to 20.0 ng/l, at E1 and E2, respectively. The individual PAH and NPAH concentrations showed

higher values at Esmailia canal sites (E1 and E2) than those at Nile River sites (NR1, NR2 and NR3) with the decreasing order of E2 > E1 >> NR1 > NR3 > NR2 (Tables 1 and 2).

The PAH and NPAH levels at all investigated sites in Nile River and Esmailia canal showed that low molecular weight (LMW) (2-3 ring) PAHs (Nap, Ace, Fle and Phe) and medium molecular weight (MMW) (4 ring) PAHs (Frt, Pyr, BaA and Chr) have higher concentrations over the high molecular weight (HMW) (5-6 ring) PAHs (Bb, BKF, Ba, DBA, Bghipe and IDP). Whereas, the LMW (2-3 ring) NPAHs (2-NF, 9-Nph and 9-NA) and MMW (4 ring) NPAHs (3-NFR, 1-NP, 6-NC and 7-NBaA) have higher concentrations over the HMW (5 ring) NPAHs (6-NBaP) (Table 3).

4 DISCUSSION

4.1 Seasonal variation of PAHs and NPAHs

The average concentrations of PAHs and NPAHs were much higher at Esmailia canal sampling sites (E1 and E2) than those at Nile River sampling sites (NR1, NR2 and NR3) in both summer and winter seasons as shown in Tables 1 and 2. The significant high levels at the former sites might be attributed to the presence of many industrial facilities along the canal including petroleum and petroleum derivatives industries discharging their wastewater without treatment to the Esmailia canal [18].

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The seasonal variation pattern (winter > summer) might be attributed to the following four factors; (i) The atmospheric fallout from vehicle exhaust can cause a significant accumulation of PAHs and NPAHs in the aquatic environment, where the meteorological conditions greatly influence fallout, particularly local fallout. So, the atmospheric winds in winter season are able to bring fallout over large areas. (ii) The inputs of PAHs and NPAHs to water environment increase because of increasing the agricultural burning for waste disposal in winter season. (iii) The warming activities, that emit PAHs and NPAHs, especially in rural areas increase also in winter at low temperatures. (iv) PAHs and NPAHs are easily decomposed at high temperatures and photo chemically degraded in the presence of sunlight in summer season [12], [27].

The ring distribution of PAHs in summer and winter season over all Nile River and Esmailia canal sites showed that the LMW PAHs and NPAHs were the predominant components in both summer and winter seasons. PAHs ring distribution followed the order of 3-ring > 2-ring > 4-ring > 5-ring > 6-ring, except for NR1 and NR2 in winter season the order was 3-ring > 4-ring > 2-ring > 5-ring > 6-ring. Whereas NPAHs had the order of 3-ring > 4-ring > 5-ring. These results can be attributed to (i) the

lower concentrations of HMW PAHs and NPAHs in the atmosphere and (ii) the lower solubility of HMW PAHs and NPAHs in water environment (Figs. 2A, B, C and D).

The concentration ratios of ［LMW］/［HMW］ PAHs and NPAHs in winter season were higher than those in summer season at all investigated sampling sites (Figs. 3A and B) that might be due to the following three reasons: (i) The lower degrees of water temperature in winter season exhibits higher concentration values. These higher levels correspond to the increase in the dissolved PAHs and NPAHs, which probably as a consequence of the atmospheric condensation. (ii) PAHs and NPAHs are easily photo chemically degraded in the presence of sunlight in summer [33], [42]. The seasonal degree of temperature in Egypt were varied from (8 – 22 ^{o}C) in winter and from (28 – 45 ^{o}C) in summer season, and the average sunlight hours in winter season is about 9 hours, whereas, it is about 13 hours in summer season [48].

The seasonal average concentrations of PAH and NPAH at Nile River sites showed higher values at NR1 site over the other two sampling sites NR2 and NR3, this can be due to the heavy traffic density as well as the close of this site to the industrial areas in Shubra El Kheima, that may lead to huge amount of PAH emissions. Whereas, at Esmailia canal sites, E2 had higher PAH and NPAH values over E1, this also can be attributed to the presence of many industrial facilities as well as oil companies discharging their waste to the Esmailia canal near to this site.

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4.2 Source identification and molecular diagnostic ratios

In recent years, several diagnostic ratios and multivariate statistical analysis methods have been used to identify possible emission sources of PAHs and NPAHs in the atmosphere [28], [3], [13]. The most widely used diagnostic ratios are Frt/Pyr, Frt/Pyr+Frt, 1-NP/Pyr and 6-NC/Chr. This is the first report to discuss the PAH and NPAH source origin in the water environment in Egypt. We compared the molecular diagnostic ratios of the water sites in this study with atmospheric sites El Dokki and El Teppen in our previous study [27] (Table 4).

Where, [Frt]/[Frt + Pyr] < 0.4 indicates petrogenic source, while [Frt]/[Frt + Pyr] > 0.4 indicates crude oil and/or wood/grass/coal combustion sources [6], [4]. For the Nile River sites (NR1, NR2 and NR3), [Frt]/[Frt+Pyr] were around 0.3 to 0.4 in both summer and winter seasons, indicating mainly petrogenic source contribution in both seasons. Whereas, those for Esmailia canal sites (E1 and E2) were around 0.6 to 0.7, indicating a mixed source contribution.

The concentration ratios of mono-NPAHs to their corresponding PAHs such as [1-NP]/[Pyr] and [6-NC]/[Chr] were effectively used to investigate the source origin in the following increasing order,

wood particulates < CEP < DEP (Tang et al., 2005). The [1-NP]/[Pyr] for Nile River sites were ranged from 3×10^{-3} to 4×10^{-3} and from 3×10^{-4} to 2×10^{-3} in summer and winter seasons, respectively. The relatively lower values of Esmailia canal sites over Nile River sites indicating a mixed contamination of CEP with petroleum sources at Esmailia canal and petrogenic sources contaminated with CEP (open air burning) inputs at Nile River sites. [Frt]/[Pyr] (m = 202) were used to differentiate between pyrogenic and petrogenic sources [6], [34]. Sicre et al. (1987) found that a [Frt]/[Pyr] < 1 was attributed to petrogenic sources and values greater than 1 were obviously related to a pyrolytic origin. [Frt]/[Pyr]values for Nile River sites were slightly lower than 1 indicating a combined contamination of petrogenic source origin polluted with pyrogenic source with the predominance of petrogenic sources at River Nile sites, whereas for Esmailia canal sites [Frt]/[Pyr] values were slightly higher than 1, indicating a predominance of pyrogenic source origin contaminated with petrogenic source at Esmailia canal sites, these values are in agreement with our above mentioned investigations.

Since an abundance of HMW PAH (e.g 5- and 6-ring) species is typically a characteristic of pyrogenic origin while LMW PAHs (e.g. 2- and 3-ring species) are more abundant in petroleum source, ratios of low molecular weight (LMW)/high molecular weight (HMW) were calculated to further distinguish petroleum from combustion source inputs. LMW/HMW ratios >1 indicate petroleum source while values <1 imply combustion [43], [26].

In this study, the concentration ratios of [LMW]/[HMW] PAHs and NPAHs in summer and winter seasons were >1 referring to the abundance of LMW PAHs and petrogenic source contamination (Figs. 3A and B), but also there were considerable amounts of HMW compounds indicating an inputs of both petrogenic and pyrogenic origin with the predominance of petrogenic sources as a combined origin from both petrogenic and pyrogenic sources. These results are in agreement with Chen et al., (2005) and Aichner et al., (2007).

4.3 Risk assessment of potential toxic fraction of PAHs and mutagenic activity of PAHs and NPAHs in the water environment

BaP has been regarded as the compound with the most important consequences for human health because of its potent carcinogenicity that classified in group 1 [17]. BaP is considered to be a sufficient index for PAH carcinogenicity. This compound has been widely used as an indicator for the environmental quality and for overall PAH carcinogenicity [45], [46]. The average concentrations of BaP at Nile River sites were varied from 18.8 to 56.8 ng/l. Whereas, at Esmailia canal sites they varied

from 71.6 to 242.1 ng/l in both seasons indicating high inputs of organic contaminants to Esmailia canal sites over Nile River sites in both summer and winter seasons.

The carcinogenicity classifications verified by EPA carcinogenicity risk assessment endeavor work group [16], [40] showed that BaA, BbF, BaP, DPA and IND are considered possibly human carcinogens that classified in group 2B, whereas other PAHs are not yet classified as promoters of the same health risk. For the carcinogenic PAH compounds the following formula was introduced [9] to calculate the BaP-equivalent carcinogenic power (BaPE):

$$BaPE = BaA * 0.06 + BbF * 0.07 + BaP + DBA * 0.6 + IND * 0.08 \quad (1)$$

In this study, the BaPE values were ranged from 65.6 to 81.3, 19.9 to 37.9 and 26.2 to 20.5 ng/l for NR1, NR2 and NR3 respectively in summer and wither seasons. The seasonal concentrations of BaBE were higher at NR1 (Cairo) site over the other two sampling sites along Nile River (NR2 and NR3). Whereas, they ranged from 87.7 to 136.7 and 342.8 to 378.9 for E1 and E2 respectively, showing higher BaPE values at E2 over E1 in both summer and winter seasons. These values indicate the dominance of BaPE values in winter than in summer season at all the investigated sites. In addition, these results underline and confirm the importance of BaP as a surrogate compound for PAHs mixture.

Since BaP and BaPE can be applied only to evaluate the risk assessment for PAHs and not for NPAHs. However NPAHs are considered to be the main causes of the direct acting mutagenicity [51]. So, in this study we investigate the total mutagenicity for PAHs and NPAHs to confirm our finding of risk assessment from BaP and BaPE. The total mutagenicity values can be obtained from the following equation:

$$\text{Total mutagenicity} = f \times c \quad (2)$$

where f is the mutagenicity factor and c is the concentration of each PAH or NPAH

For all sampling sites, the total indirect and direct mutagenicity values in winter season calculated by PAHs and NPAHs, respectively, were higher than those in summer at all investigated sites. The indirect mutagenicity values calculated by PAHs at Nile River sites NR1, NR2 and NR3 at summer and winter seasons were varied from 65.6 to 83.2, from 26.4 to 38.2 and from 33.3 to 33.4 revertants/l, respectively. However those for the direct mutagenicity values calculated by NPAHs were varied from

22.7 to 25.9, from 14.8 to 17.6 and from 14.0 to 16.5 revertants/l, respectively in summer and winter seasons. For Esmailia canal sites E1 and E2, the PAH indirect mutagenicity in summer and winter seasons were varied from 179.5 to 222.3 and from 412.9 to 538.1 revertants/l, respectively. Whereas, those for NPAH direct mutagenicity were varied from 22.3 to 25.9 and from 40.3 to 49.8 revertants/l, respectively, in summer and winter seasons. The highest PAH and NPAH mutagenicity along Nile river sites were detected at NR1, whereas E2 showed higher values over E1 at Esmailia canal sites. The seasonal values of the both indirect and direct mutagenicity for both Nile River and Esmailia canal sites showed the same order as follow:

In summer: E2 > E1 > NR1 > NR3 > NR2; in winter: E2 > E1 > NR1 > NR2 > NR3.

These results indicated that the risk assessment of the mutagenic compounds PAHs and NPAHs in winter season were higher than that in summer season at all investigated sites, and these results were matched with those obtained from the atmospheric sampling sites El Dokki and El Teppen [27] that are close to these water sampling sites specially NR1, E1 and E2.

5 CONCLOSION

► Fifteen PAHs and eight NPAHs were determined at three sites along Nile River (NR1, NR2 and NR3) and other two sampling sites along Esmailia canal (E1 and E2) in summer and winter seasons.

► The concentrations of PAHs and NPAHs were higher in winter than in summer at all sites.

► The concentration order for all sampling sites was E1 > E1 >> NR1 > NR3 > NR2.

► Ring distribution of PAHs was in the order of: 3-ring > 2-ring > 4-ring > 5-ring > 6-ring. Whereas, NPAHs are in the order of 3-ring > 4-ring > 5-ring, at all investigated sites in summer and winter seasons, indicating the predominance of LMW (2-3 ring) compounds over the HMW (5-6 ring) compounds.

► The ratios of [Frt]/[Frt + Pyr], [Frt]/[Pyr] and [1-NP]/[Pyr] indicated the predominance of petrogenic source origin contaminated with pyogenic source at Nile River sites, whereas at Esmailia canal sites there was a predominance of pyrogenic source origin contaminated with petrogenic source in both summer and winter seasons.

► BaP equivalent carcinogenic power of PAHs and mutagenic activities of PAHs and NPAHs showed higher values in winter than in summer season at all the investigated sites.

► The seasonal indirect and direct mutagenicity calculated by PAHs and NPAHs respectively at Nile River and Esmailia canal sites showed the same order as follow:

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In summer: E2 > E1 > NR1 > NR3 > NR2; in winter: E2 > E1 > NR1 > NR2 > NR3.

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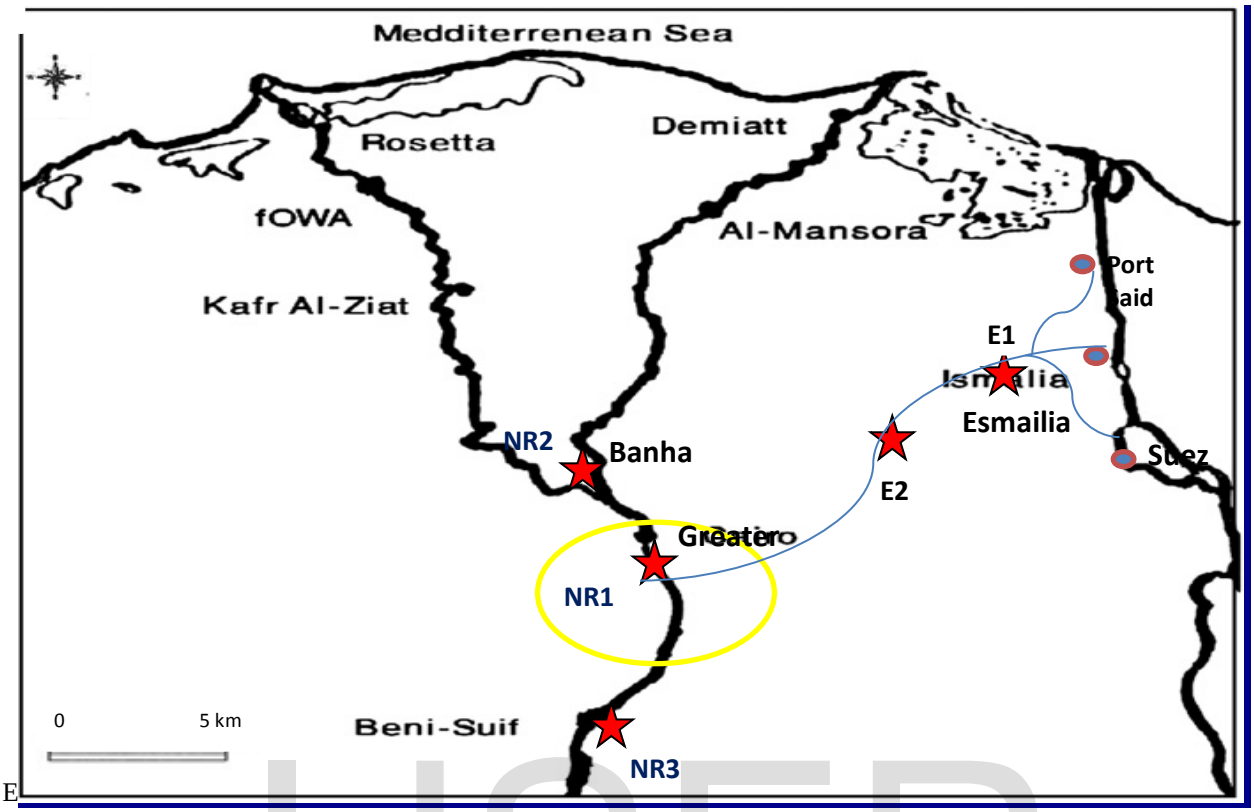

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Fig 1. *Sampling sites along the Nile River and Esmailia canal.*

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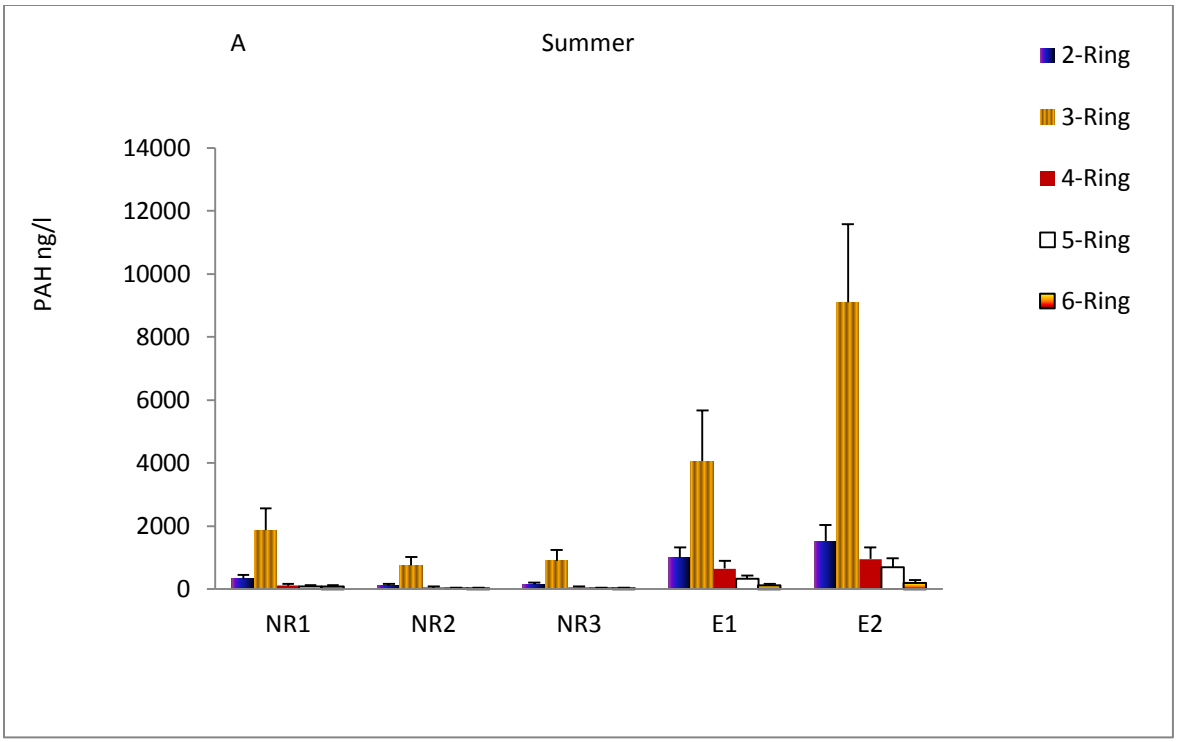
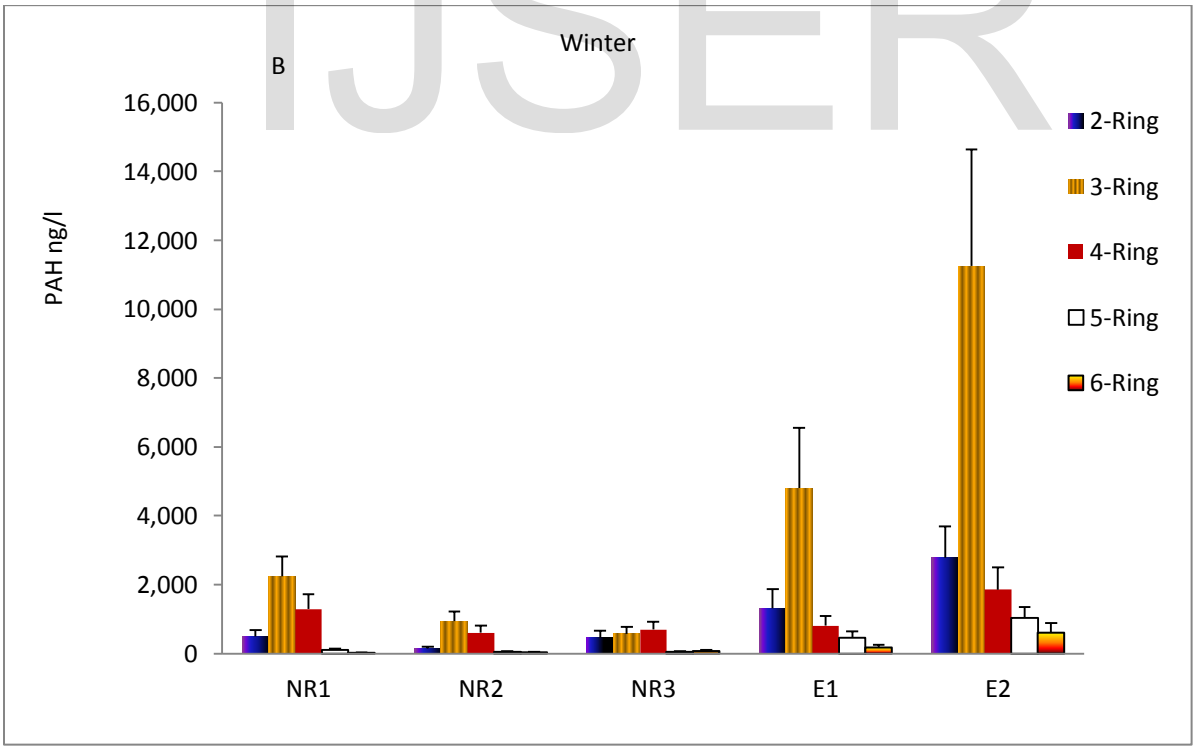
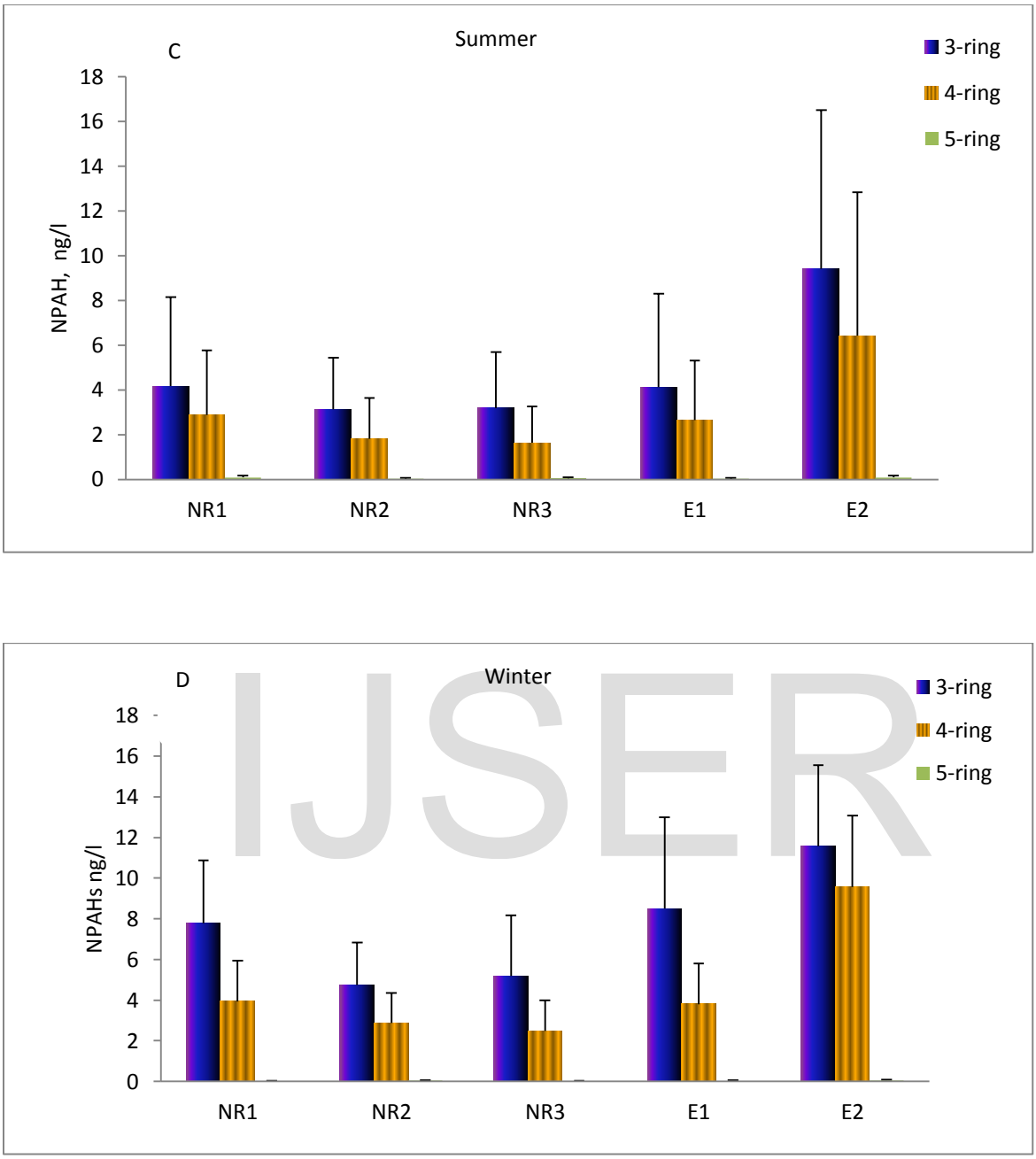

A
Summer
2-Ring
3-Ring
4-Ring
5-Ring
6-Ring
PAH ng/l
14000
12000
10000
8000
6000
4000
2000
0
NR1
NR2
NR3
E1
E2

IJSER


B
Winter
2-Ring
3-Ring
4-Ring
5-Ring
6-Ring
PAH ng/l
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
NR1
NR2
NR3
E1
E2



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Figs. 2. *Comparison of ring number distributions of PAHs and NPAHs at Nile River and Ismailia canal sites in summer and winter seasons.*
A, summer PAHs; B, winter PAHs; C, summer NPAHs; D, winter NPAHs

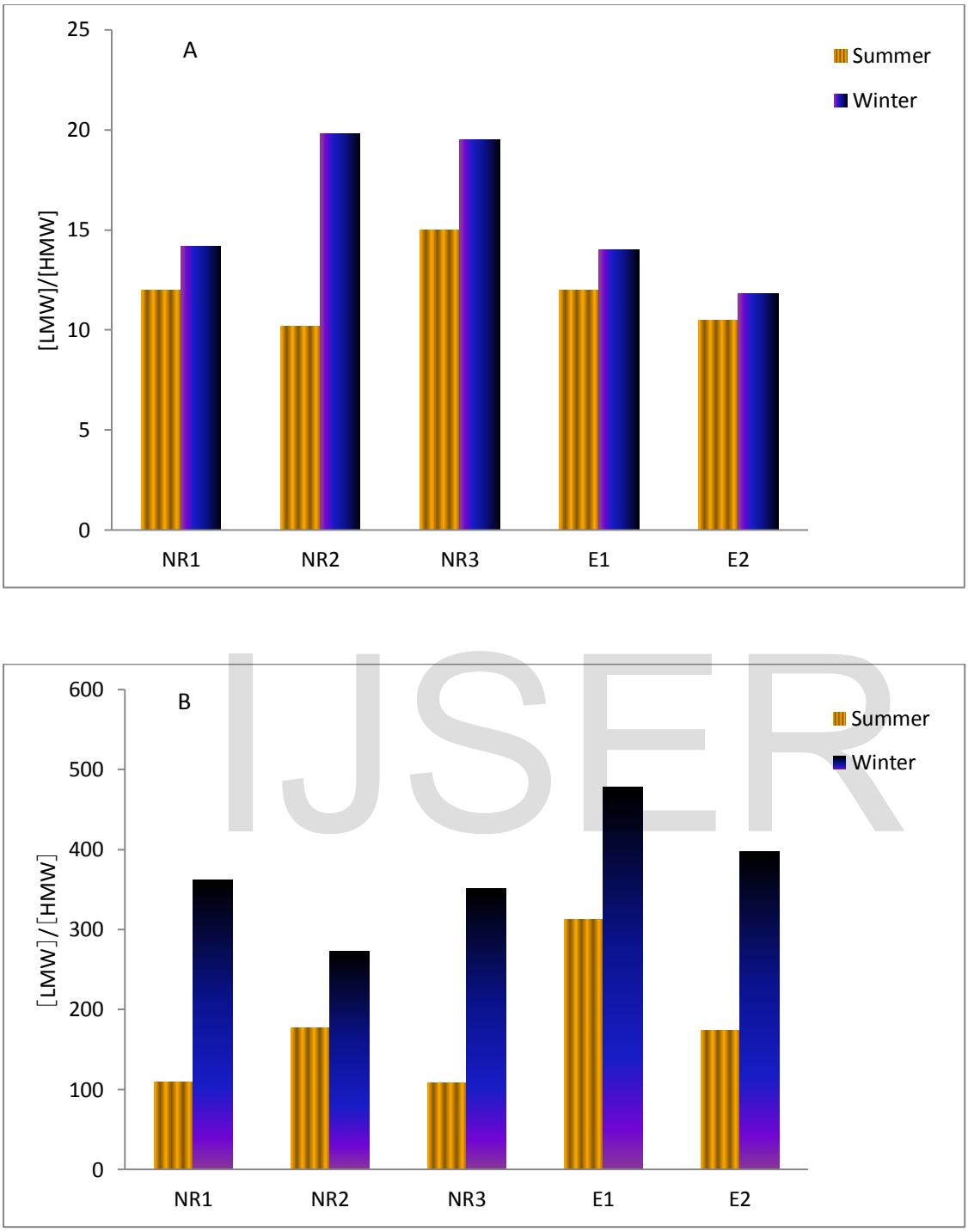

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Fig. 3. *Comparison of [LMW]/[HMW] ratios of PAHs and NPAHs at Nile River and Esmailia canal sites in summer and winter.*
(A) PAHs, (B) NPAHs.
LMW PAHs = Nap , Ace , Fle , Ant , Phe , Frt, Pyr, BaA and Chr .
HMW PAHs = BbF , BkF , BaP , Bghipe and IDP.
LMW NPAHs = 2-NF , 9-Nph , 9-NA , 3-NFR , 1-NP , 6-NC and 7-NBaA .
HMW NPAHs = 6-NBaB.

Table 1.

PAH and NPAH concentrations values at Nile River and Esmailia canal sites in summer season.

		NR 1				NR 2				NR 3				E1				E2			
		min	Max	ave	std	min	max	ave	std	min	max	ave	std	Min	Max	ave	std	min	Max	ave	std
	PAH (ng/l)																				
2-ring	Nap	228.3	483.5	329.0	158.0	89.0	145.0	115.5	47.1	96.5	198.5	152.9	69.0	860.0	1380.0	998.6	371	1256	1992	1528.6	705
	Ace	614.0	1012.0	808.8	288.0	221.0	427.0	320.4	144.6	277.0	636.0	424.7	179.0	1050.0	1713.0	1401.3	511	3900	5119	4516.3	1980
3-ring	Fle	71.0	186.4.3	129.9	59.0	30.1	78.0	46.1	19.6	21.0	77.8	52.8	17.0	410.0	781.0	668.3	293	787	1314	1058.1	402
	Phe	611.0	1121.0	930.2	298.0	299.0	481.0	391.0	188.0	298.0	514.0	432.9	166.0	1780.0	2259.0	2058.5	989	2110	4321	3671.5	1311
	Ant	1.9	5.2	3.6	1.3	0.8	3.8	2.0	0.8	1.0	4.7	2.1	0.8	12.6	33.1	20.4	9.1	18.2	44.9	35.8	15.1
	Frt	23.5	52.6	37.5	13.2	13.6	33.0	18.3	9.2	11.9	33.6	22.5	7.0	198.0	405.7	300.4	123	407	690.5	518.1	211
4-ring	Pyr	42.5	77.0	56.8	21.2	19.1	44.9	30.6	11.8	18.4	54.9	32.0	11.3	188.0	302.0	240.1	102	182	331.2	272.2	114
	BaA	3.3	15.0	8.0	3.0	4.0	11.2	7.2	2.6	3.9	16.1	9.2	3.7	23.5	51.7	37.4	14.2	36.9	90.7	68.5	30.2
	Chr	7.1	16.4	11.8	4.5	0.8	5.4	2.9	1.1	2.1	8.6	5.2	2.0	59.0	101.0	80.9	27.4	59.6	131.2	98.6	41
	BbF	10.1	23.0	16.9	6.0	3.5	16.1	10.2	2.9	5.3	20.1	13.0	4.1	92.0	167.5	135.5	59.2	113	314.3	237.1	109
5-ring	BkF	1.3	4.8	3.7	1.3	0.9	4.5	2.2	0.9	ND	6.1	3.1	1.2	13.8	55.0	31.3	12.3	36.1	99.2	67.1	28.9
	BaP	31.5	66.0	45.5	15.3	14.0	31.1	18.8	9.0	11.2	33.2	24.7	10.0	42.0	94.6	71.6	30.2	187	301	242.1	99.6
	DBA	17.1	38.0	27.0	9.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	89	152.1	121.7	49.8
	BghiPe	18.0	49.5	35.0	12.0	9.8	39.0	23.3	9.3	4.1	26.5	14.6	6.5	38.0	91.0	70.0	28.6	94.5	177.3	140.0	56.7
6-ring	IDP	15.3	40.8	27.4	11.0	ND	ND	ND	ND	ND	ND	ND	ND	38.7	77.0	54.9	20.1	46.8	131	96.0	41.1
	Tot			2471.2	901.6			988.4	416.9			1189.6	437.6			6168.8	2509			12671.7	5094.4
	NPAH (ng/l)																				
	2-NF	1.33	3.45	2.75	1.32	0.68	2.43	1.98	1.10	ND	3.98	2.13	1.20	1.46	4.71	2.78	1.22	2.23	8.98	6.69	2.99
3-ring	9-Nph	0.97	1.74	1.18	0.63	0.50	1.61	0.99	0.42	0.40	1.65	0.91	0.44	0.68	2.56	1.10	0.56	1.21	4.05	2.31	1.21
	9-NA	ND	0.38	0.24	0.15	ND	0.26	0.17	0.06	0.05	0.22	0.15	0.06	ND	0.51	0.23	0.11	0.20	0.76	0.42	0.22
	3-NFR	1.33	3.1	2.51	1.22	0.91	1.98	1.46	0.65	1.12	2.43	1.81	0.86	1.88	3.45	2.82	1.32	3.48	7.32	5.01	2.42
4-ring	1-NP	0.06	0.18	0.11	0.05	0.02	0.11	0.06	0.03	0.04	0.23	0.09	0.04	ND	0.16	0.07	0.03	0.15	0.44	0.24	0.15
	6-NC	0.22	0.88	0.52	0.21	0.19	0.48	0.36	0.16	0.19	0.61	0.42	0.25	0.20	0.85	0.50	0.26	0.38	1.78	1.08	0.60
	7-NBaA	0.05	0.21	0.15	0.05	0.09	0.28	0.18	0.06	0.10	0.44	0.20	0.12	0.03	0.24	0.13	0.06	0.16	0.68	0.30	0.66
5-ring	6-NBaP	0.03	0.12	0.08	0.03	ND	0.08	0.03	0.02	ND	0.18	0.05	0.02	ND	1.01	0.03	0.01	0.04	0.16	0.09	0.04
	Tot.			7.54	3.2			5.23	2.1			5.71	2.4			7.62	3.3			15.96	7.1

ND; not detected

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Table 2.

PAH and NPAH concentration values at Nile River and Esmailia canal sites in winter season.

		NR 1				NR 2				NR 3				E1				E2			
		min	max	ave	std	min	max	ave	std	min	max	ave	std	min	max	ave	std	min	max	ave	std
	PAH (ng/l)																				
2-Ring	Nap	341.2	618.0	481.8	202.0	108.0	178.6		60.2	122.4	218.5	176.1	71.8	978.0	1630.5	1322.6	621.2	2011.4	2822.0	2575.4	1100.3
	Ace	905.7	1211.0	1073.0	435.9	365.2	547.8	449. 2	200.7	389.0	654.5	504.5	200.5	1223.4	1995.6	1753.7	800.0	3120.5	3951.2	3683.5	1220.0
3-Ring	Fle	211.5	302.6	259.9	111.2	38.5	78.7	59.4	21.9	59.1	128.7	91.0	39.0	605.2	990.6	872.5	410.3	1995.6	2516.0	2305.6	980.8
	Phe	897.9	1168.3	1012.5	369.1	386.5	491.2	436.3	199.5	411.0	641.3	510.3	199.2	1961.2	2419.4	2247.3	1006.3	4780.2	5931.4	5400.2	2055.2
	Ant	3.8	8.3	5.3	2.1	0.4	5.8	2.6	1.2	1.2	4.6	2.4	1.1	14.3	32.1	24.6	10.2	34.5	79.3	61.3	25.1
	Frt	29.1	61.5	45.1	21.0	9.5	29.1	18.8	8.7	8.3	40.2	22.5	9.9	385.4	506.2	424.3	198.4	681.6	1121.7	976.2	400.2
4-Ring	Pyr	38.9	89.6	69.9	29.3	24.1	60.2	37.8	16.5	22.5	54.5	34.9	14.5	205.3	298.1	251.8	109.0	411.8	700.3	528.3	211.4
	BaA	6.7	15.7	9.6	3.4	4.3	10.6	7.2	3.0	2.9	17.5	8.0	3.1	28.6	59.5	33.4	13.7	49.7	132.0	105.1	42.9
	Chr	11.9	27.3	14.7	5.6	1.6	6.2	3.7	1.5	1.2	7.4	3.7	1.9	69.5	122.4	98.6	40.2	189.5	281.1	247.2	110.5
	BbF	9.2	43.0	20.3	8.7	12.1	34.3	19.2	9.8	5.5	28.6	13.5	6.0	98.6	167.7	149.0	62.5	231.2	413.4	345.4	135.1
5-ring	BkF	3.6	11.5	6.0	2.4	3.1	12.0	6.7	3.1	1.4	11.0	6.0	2.7	16.5	49.8	34.3	13.9	88.5	139.1	117.0	49.9
	BaP	28.7	77.9	56.8	21.9	16.2	44.8	25.0	12.0	10.8	29.5	17.9	7.9	41.5	95.1	73.3	29.8	125.9	242.7	203.5	91.6
	DBA	12.8	51.5	33.8	14.6	9.0	29.5	16.9	7.7	ND	ND	ND	ND	32.8	91.3	74.4	25.9	130.0	265.2	216.3	98.5
6-Ring	BghiPe	41.0	98.5	87.5	38.1	11.0	44.8	21.5	11.2	7.6	44.5	23.3	10.5	65.1	128.0	105.0	42.1	198.5	355.7	303.4	129.1
	IDP	8.6	40.8	27.4	12.2	3.6	18.5	12.2	7.1	ND	28.7	13.7	5.6	57.0	100.5	82.3	32.5	141.5	257.3	205.8	97.5
	Tot			3203.6	1177.5			1266.4	464.1			1427.9	473.7			7547.1	3116.2			17274.2	5748.1
	NPAHs (ng/l)																				
	2-NF	2.03	7.81	6.24	3.02	1.21	4.81	3.66	1.71	1.68	5.07	3.99	1.92	2.75	8.69	7.04	3.02	3.98	9.47	8.59	4.21
3-Ring	9-Nph	0.95	2.81	1.27	0.67	0.47	1.55	0.89	0.42	0.76	1.72	1.02	0.60	0.54	1.43	1.19	0.62	1.77	3.12	2.43	1.25
	9-NA	0.06	0.39	0.27	0.13	ND	0.27	0.19	0.10	0.05	0.21	0.17	0.05	0.12	0.38	0.26	0.14	0.28	0.79	0.54	0.21
	3-NFR	1.77	3.11	2.73	1.31	1.01	1.98	1.52	0.71	1.13	2.48	1.82	0.82	1.69	3.18	2.41	1.15	3.01	7.88	6.32	3.1
4-Ring	1-NP	0.09	0.32	0.18	0.06	ND	0.22	0.14	0.06	0.04	0.23	0.14	0.05	0.06	0.25	0.17	0.60	0.24	0.56	0.35	0.17
	6-NC	0.21	0.59	0.46	0.21	0.18	0.55	0.37	0.17	ND	0.68	0.31	0.21	0.26	0.69	0.44	0.25	0.44	1.37	0.95	0.43
	7-NBaA	0.14	0.39	0.22	0.13	0.07	0.31	0.20	0.11	0.10	0.24	0.19	0.10	0.15	0.29	0.22	0.12	0.31	0.59	0.46	0.26
5-Ring	6-NBaP	ND	0.09	0.03	0.02	ND	0.10	0.04	0.02	0.01	0.03	0.02	0.01	ND	0.05	0.03	0.18	0.02	0.10	0.06	0.03
	Tot.			11.18	5.1			6.99	3.2			8.01	3.4			11.76	5.1			19.96	8.9

ND; not detected

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Table 3.

Percentage of LMW, MMW and HMW PAH compounds at Nile River and Esmailia canal sites in summer and winter seasons.

Compound	NR1				NR2				NR3				E1				E2			
	Summer	%	Winter	%	Summer	%	Winter	%	Summer	%	Winter	%	Summer	%	Winter	%	Summer	%	Winter	%
PAHs																				
LMW	2201.5	89.0	2832.6	88.0	875.0	88.0	1092.9	86.0	1065.4	89.0	1284.3	90.0	5146.7	83.0	6220.7	81.0	10810	85.0	14026.0	81.0
MMW	207.0	8.0	256.1	7.0	90.2	10.0	135.3	11.0	109.6	9.0	106.5	7.0	897.2	14.0	1139.0	16.0	1625.3	12.0	2739.0	14.0
HMW	62.4	3.0	115.0	5.0	23.3	2.0	33.7	3.0	14.6	1.0	37.1	3.0	124.9	3.0	187.3	3.0	236.1	3.0	509.2	5.0
NPAHs																				
LMW	4.96	65.0	6.80	61.0	3.14	64.0	4.50	59.0	3.39	59.0	5.28	67.0	4.11	61.0	8.05	68.0	9.42	59.0	11.06	55.0
MMW	2.58	34.0	3.94	34.5	2.00	39.5	2.48	29.0	2.20	29.0	2.58	32.7	2.65	38.0	3.70	31.0	6.43	40.5	9.00	44.0
HMW	0.08	1.0	0.06	0.5	0.03	0.3	0.03	3.0	0.05	4.0	0.05	0.5	0.03	1.0	0.07	1.0	0.09	0.3	0.20	4.0

LMW, 2-3 ring; MMW, 4-5 ring; HMW, 6- ring

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Table 4.

Molecular diagnostic ratios at sampling sites (El dokki and El Teppen) and water sampling sites (NR1, NR2, NR3, E1 and E2) in summer and winter seasons.

		Summer				Winter			
Sample	Sampling site	[Frt]/[Pyr]	[Frt/[Frt] + [Pyr]	[1-NP]/[Pyr]	[6-NC]/[Chr]	[Frt]/[Pyr]	[Frt/[Frt] + [Pyr]	[1-NP]/[Pyr]	[6-NC]/[Chr]
Airborn	* Dokki	0.9	0.5	5×10^{-3}	1×10^{-3}	0.8	0.3	3×10^{-2}	3×10^{-2}
	* Tepen	1.7	0.6	6×10^{-4}	1×10^{-3}	1.4	0.7	$3x\ 10^{-2}$	1×10^{-2}
Water	** NR1	0.8	0.3	3×10^{-3}	3×10^{-2}	0.8	0.4	2×10^{-3}	2×10^{-2}
	** NR2	0.6	0.3	4×10^{-3}	11×10^{-2}	0.7	0.1	3×10^{-3}	12×10^{-2}
	** NR3	0.8	0.4	4×10^{-3}	8×10^{-2}	0.9	0.4	3×10^{-4}	17×10^{-2}
	** E1	1.6	0.6	6×10^{-4}	4×10^{-3}	1.3	0.6	1×10^{-3}	1×10^{-2}
	** E2	2.6	0.6	7×10^{-3}	4×10^{-3}	1.9	0.8	2×10^{-3}	1×10^{-2}

(*) Air borne particulate sampling site

(**) Water sampling site

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