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Research Article

Assessment of Dissolved and Particulate Polycyclic Aromatic Hydrocarbons (PAHs) and their Nitro Derivatives (NPAHs) in the Mediterranean Sea Surface Waters along Alexandria Coast

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Abstract

Background and Objective: Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are widely diffused organic pollutant to the environment because of their semi-volatile characteristics. These pollutants are carcinogenic and/or mutagenic and have to be intensively regulated and monitored. In this research studied the dissolved and particulate PAH and NPAHs (nitro-polycyclic aromatic hydrocarbons) concentrations in the Mediterranean sea water along Alexandria coast. **Materials and Methods:** Samples were collected from three different sites (Alex1, Alex2 and Alex3) representing different activities in the sampling area. HPLC with fluorescence detection was used for PAHs detection, whereas, HPLC with chemiluminescence detection was used for NPAHs detection. **Results:** The measured concentration levels of dissolved PAHs and NPAHs were ranged from (230.5-704.1) ng L^{-1}, respectively, while those for particulate PAHs and NPAHs were ranged from (79.1-288.5) ng L^{-1}, respectively. Molecular diagnostic ratios were calculated to identify the sources of emissions of such compounds. Results indicated a major contributor of the pyrolytic and sewage discharge contamination particularly at sites (Alex2 and Alex3) with a mixed petrogenic pattern from urban runoff inputs and frequent oil spills at site (Alex1). **Conclusion:** PAHs and NPAHs total concentration levels at the three sampling stations in the Mediterranean Sea along Alexandria coast followed the order: Alex1> Alex2> Alex3.

Key words: Polycyclic aromatic hydro carbons, nitrated polycyclic aromatic hydro carbons, organic contaminants, wastewater, oil spills

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Competing Interest: The author has declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Numerous organic chemicals accumulate at the sea surface particularly those showing a strong partitioning affinity. Many of hydrophobic organic pollutants like PAHs and their nitro derivatives can concentrate in the water surface. These compounds can exhibit increased solubility with elevated dissolved organic matter. PAHs and their nitrated derivatives are ubiquitous bio-accumulative resistant chemicals in the environment with high toxicity characteristics[1-4]. They have a negative impact on the environment and may cause a serious threats to human health and other animals as well[5,6]. Major contributors for PAH and NPAH emissions are mainly anthropogenic sources, as the incomplete combustion, open air burning, fossil fuels pyrolysis and oil spells[3,6,7]. PAHs and their derivatives can be classified into petrogenic and pyrogenic compounds according to their emission source in the environment.

They have different degrees of carcinogenicity and/or mutagenicity related to their abundance and concentration levels in the environment[3,8]. The fate and distribution of such contaminants have been studied to determine their emission sources and pathway in the environment[9-12]. PAHs and their derivatives can travel over large distances after releasing to the outer atmosphere then can be condensed and fall down causing water bodies contamination.

They also can reach water systems through several pathways like oil spills and industrial effluents discharge. The major input of PAHs and NPAHs to the water system mainly comes from the atmosphere through urban runoff and inputs from tributaries causing the exchange of low molecular weight (LMW) 2-4-ring PAHs and NPAHs from air to water[3,6,13,14]. The solubility of PAHs in water systems is very low, therefore their abundance in the aquatic environment is mainly in particulate phase especially for high molecular weight (HMW) PAHs. Whereas, LMW compounds are effectively show more solubility characteristics and higher abundance in dissolved phase particularly in surface water system[8]. Therefore, the concentration of dissolved and particulate PAHs and their nitro derivatives in water is often depending on the molecular weight magnitude. Due to the abovementioned features of PAHs and their derivatives, the accurate measurements, detection of both dissolved and particulate PAH compounds in water system is not so easy due to encountering of several sampling obstacles.

Mediterranean sea is a semi-closed sea that receives a lot of contaminants from the surrounding highly populated areas that may cause a low capacity of water portioning with the Atlantic Ocean. Recently, with increasing the human developments and activities, the coastal areas are greatly influenced by several contaminants enhancement. Moreover, it provides several examples reflecting the negative impacts of anthropogenic sources of organic contaminants on the Mediterranean sea coastal area[9,3,12].

The objectives of the study were to (1) Determine total and average concentration levels of PAHs and their nitrated derivatives in dissolved and particulate forms, (2) Reveal the distribution pattern of dissolved and particulate PAHs and NPAHs in the surface seawater from Mediterranean sea along Alexandria coast, (3) Investigation of major contributors and potential sources of PAHs and NPAHs in Mediterranean sea along Alexandria coast.

MATERIALS AND METHODS

Sampling: Sea-surface micro-layer water samples were collected at three different stations (Alex1, Alex2 and Alex3) from the Mediterranean sea along the Alexandria coast in 2015 during winter season. Alex1 (Ras Al Tin) was located in the Western part of the Alexandria coast. The main activities at this station are mainly motor ship maintenance center, fishing and a place for recreation. Alex2 (Raml Station), this station is a residential site located to the East of the Eastern harbor almost in the middle of Alexandria coast. This site is affected by human activities and mainly used as a recreational place. From time to time it receives sewage discharging from the close residential area. Alex3 (Qaitbay fort) it is located to the West of the Eastern harbor, it is mainly a touristic site and affected by fishing and touristic activities. This site also can be affected by the Eastern harbor and shipping activities.

Chemicals: U.S. Environmental Protection Agency (EPA610) Mixture containing 15 PAHs were purchased as PAH standard solution from Supleco (Bellefonte, PA, U.S.A). Whereas, internal standard of deuterated PAHs were purchased from Wako Pure Chemical (Osaka, Japan) and they were dissolved in acetonitrile (Kanto Chemical, Tokyo, Japan). While, NPAHs solutions were purchased from Aldrich (Chemical) (Milwaukee, WI, U.S.A.) All other chemicals used were of analytical reagent grade.

Extraction: The collected (4L) surface water samples from the stations were filtered for dissolved phase (DP) and particulate phases (PP) PAHs and NPAHs. Among all PAHs we select [acenaphthylene (Ace), fluorene (Fle), anthracene (Ant), fluoranthene (Flu), Pyr,benz[a] anthracene (B[a] A), chrysene

(Chr), benzo[b] fluoranthene (B[b] F), benzo[k]-fluoranthene (B[k] F), B[a] P, dibenz[a,h] anthracene (DBA), benzo[ghi] perylene (BPe) and indeno[1,2,3-cd] pyrene (IDP)]and for NPAHs [6-nitrochrysene (NC) and 1-nitropyrene (1-NP), 2-nitrofluorene (2NF) and 3-nitrobenzanthrone, 9-nitroanthracene (9-NA), 7-nitrobenz[*a*]anthracene (7-NBaA), 6-nitrobenzo[*a*]pyrene (6-NBaP)].

For PAHs, samples were filtered through a glass fiber membrane (pore size 0.5 µm, Advantech, Tokyo, Japan) into the glass bottle with methanol to collect the dissolved phase (DP)-PAHs. The particulate phase (PP)-PAHs were retained on the glass fiber membrane.C18 cartridges (Waters Sep-Pak plus C18 Cartridge (820 mg), Milford, MA, U.S.A). 15 mL of dichloromethane-water (1:9, v/v), 15 mL of methanol-water (1:9, v/v) and 15 mL of methanol-water (1:9, v/v) at a flow rate of about 10 mL min^{-1} were successively used for filter paper pre conditioning, then dried overnight before use. While, For PP-PAHs, 50 mL of dichloromethane through the glass fiber membrane twice, the nan internal standard solution 20 µL was spiked with the (4L) DP and PP fractions, then solid phase extraction was applied to the filtrate using the pre conditioned C18 cartridge at a flow rate of about 10 mL^{-1}. C18 cartridge was eluted with 15 mL of dichloromethane, then a drop of dimethyl sulfoxide (DMSO) was added to the eluate, then solution was evaporated. After evaporation, the residual volume was dissolved in 1 mL of n-hexane and then cleaned up through a silica gel cartridge (Waters, Milford, MA, U.S.A.). 5 mL of n-hexane was used for washing the cartridge, then 15 mL of the mixture of n-hexane-acetone (9: 1, v/v) PAHs were applied to the elute. Finally, the eluate was evaporated and the residual volume was dissolved in 800 µL of acetonitrile and stored in -20°C Frigidaire until HPLC assay.

For NPAHs, 100 µL of FNF (10 µmol L^{-1} dissolved in acetonitrile) was added to the filtrate and the solution was filtered through C18 3M Empore disk (Bioanalytical Technologies, St. Paul, MN, U.S.A.) preconditioned using 40 mL of methanol, 20 mL of dichloromethane and 20 mL of water, at a flow rate of 300 mL min^{-1} to collect dissolved NPAHs. The disk was suctioned for 20 min to completely remove all the water and then dried overnight in a desiccator wrapped in aluminum foil. The GC filter was cut into small 5 mm square pieces and put in a conical flask. After the addition of 100 µL of FNF internal standard, 20 mL of benzene and ethanol were added in the ratio of 3:1 (v/v). The mixture was super sonicated for 15 min and transferred into a separating funnel through filter paper, taking care not to transfer the cut GC filter pieces as well. The GC filter pieces in the conical flask were then super sonicated again using 20 mL of fresh benzene-ethanol (3:1, v/v), for 10 min and once more filtered via a filter paper into the separating funnel. The solutions containing PP-NPAHs were mixed in the separating funnel and then washed successively using 40 mL of 5% sodium hydroxide, 40 mL of 20% sulfuric acid and then 40 mL of distilled water, twice. Afterwards, 100 µL of dimethyl sulfoxide (DMSO) was added and the mixture was evaporated. Finally, 900 µL of ethanol was added into the residue to make 1 mL of aliquot.

The C18 disk was collected in a conical flask and then 20 mL of dichloromethane was added. The disk was super sonicated for 10 min and the dichloromethane solution was transferred into a round-bottomed flask through a filter paper. The disk was super sonicated again with 20 mL of dichloromethane for another 10 min. The solutions containing DP- NPAHs were again collected in the round-bottomed flask. After 100 µL of DMSO was added, the mixture was evaporated away. Finally, 900 µL of ethanol was added into the residue to make 1 mL of aliquot. Both sample solutions of (DP and PP) NPAHs were injected into the HPLC machine for analysis.

HPLC–MS analysis: For PAHs, HPLC with fluorescence detection was used, the system of (L series, Hitachi High Technologies, Tokyo, Japan) equipped with Inertsil ODS-P analytical (4.6 mm i.d.×250 mm, 5 µm, GL Sciences, Tokyo, Japan) and guard (4.0 mm i.d.×10 mm, 5 µm, GL Sciences) columns. Both columns were kept at 20°C in a column oven. The mobile phase (mixture of acetonitrile-water) was delivered in gradient mode with acetonitrile increasing from 55-100% over the course of 60 min. The flow rate of the mobile phase was kept at 1 mL min^{-1}. Both the excitation and emission wavelengths of the fluorescence detector were set at optimum wavelengths for each PAH with a time program.

While, for (DP and PP) NPAHs, HPLC with chemiluminescence detection with several modifications was used according to our laboratory detection method[15]. The 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). Other conditions were the same as in our previous research[9,10,15,16].

RESULTS AND DISCUSSION

The total average concentration levels of PAHs and NPAHs from the Mediterranean Sea water at three selected sites along the Alexandria coast (Alex1, Alex2 and Alex3) ranged from 309.5 to 992.6 and from 3.8 to 7.9 ng L^{-1}, respectively (Table 1). The highest concentration levels of PAHs and NPAHs were detected at the site Alex1, this may be due to mixed pyrogenic and petrogenic contamination at this site. These contaminants came from motor ships maintenance that may spill oils to the sea beside urban runoff and residential activities. The second highest concentration levels of PAH and NPAH were detected at site (Alex2) due to the presence of intense touristic and residential activities very close to this site that may discharge different wastes to the sea, besides the urban runoff inputs. The lowest concentration levels were detected at site (Alex3) due to touristic activities only (Fig. 1a, b).

There is an obvious scarcity in the literature for the data related to the occurrence of dissolved PAHs and NPAHs in the dissolved phase. This shortage of data mainly arises from the fact that PAH and their nitroderivatives are considered to occur mainly associated with particles due to their high hydrophobicity. Besides, the operational difficulties in dealing with a relatively large sample in dissolved phase. However, the dissolved concentration fractions of PAHs and their nitro derivatives have higher importance than their corresponding particulate fractions, particularly for systems with lower load of particulate matter. So, the dissolved phase concentrations play an important role in the exact assessment of actual PAHs and NPAHs concentration levels[3, 6,17].

Concentrations of (DP and PP) PAHs and NPAHs in the Mediterranean Sea from three different sites at Alexandria coast surface waters are listed in Table 2. The DP average concentrations of PAHs and NPAHs varied from 230.5-704.1 and 2.5-5.3 ng L^{-1}, respectively. These concentrations were higher than the corresponding levels of PAH and NPAH in the PP that varied from 79-288.5 from 1.7-2.6 ng L^{-1}, respectively. This implies that in the Mediterranean Sea waters the greatest PAH and NPAH fractions are present in the DPas illustrated in (Fig. 2a,b and 3a,b). The quantitative predominance of both DP and PP concentration levels is highly related to the total amount of detected PAHs and their nitro derivatives.

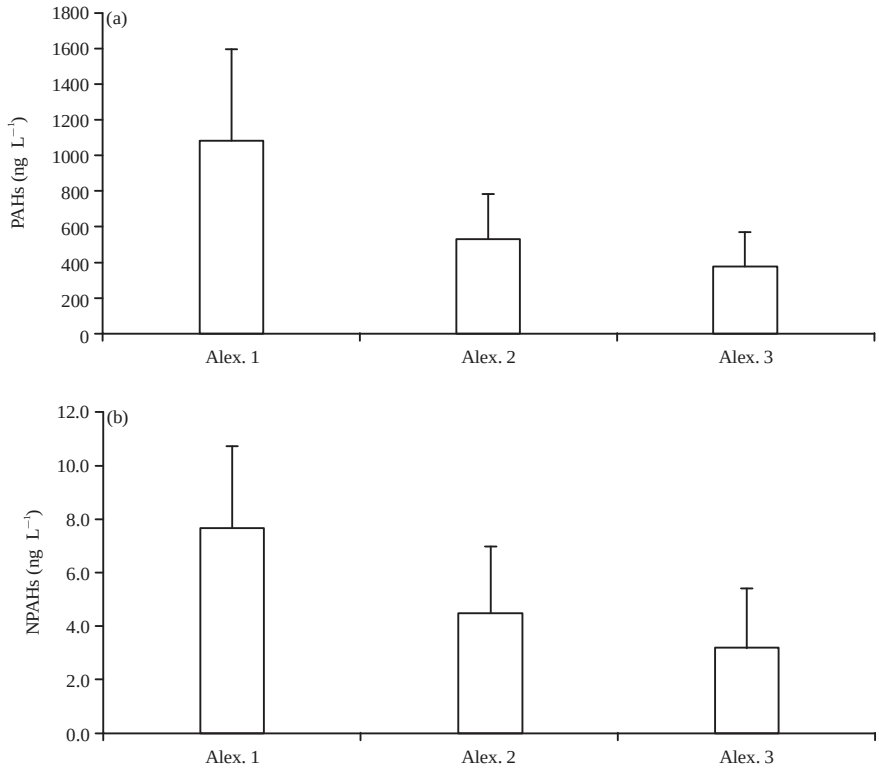

Fig. 1(a-b): Total PAH and NPAH concentrations of Mediterranean Sea water at the investigated sites along Alexandria coast (a) Total PAHs (= Frt+Pyr+BaA+Chr+BbF+BkF+BaP+BghiPe+IDP) and (b) NPAHs (= 2NF+FNF+2-NA+9-NA + 3-NBA + 1-NB + 6-NC + 7-NBaA + 6-NbaP)
Each column and vertical bar represent mean values and SD, respectively

Table 1: Concentrations of dissolved and particulate PAH and NPAH of Mediterranean sea water at the investigated sites along the Alexandria coast

		Alex1			Alex2			Alex3		
Ring no.	Short name	Dissolved	Particulate	Total	Dissolved	Particulate	Total	Dissolved	Particulate	Total
PAH (ng L^{-1})										
2-ring	Nap	262.30	41.61	303.91	89.40	10.41	99.81	68.50	7.40	75.90
3-ring	Ace	230.02	47.30	277.32	112.96	16.75	129.71	94.20	9.10	103.30
	Fle	68.07	37.44	105.51	28.93	21.70	50.63	15.53	7.50	23.03
	Phe	128.60	34.30	162.90	124.40	25.73	150.13	37.90	11.04	48.94
	Ant	0.97	3.89	4.86	0.61	0.49	1.09	0.61	0.36	0.97
4-ring	Frt	3.23	12.91	16.14	1.61	7.60	9.21	4.84	3.23	8.07
	Pyr	3.94	35.48	39.42	1.97	21.97	23.94	2.96	18.97	21.93
	BaA	2.25	4.50	6.75	1.13	1.13	2.25	1.46	0.56	2.03
	Chr	1.84	5.52	7.36	0.92	0.92	1.84	0.92	0.92	1.84
5-ring	BbF	0.39	11.72	12.11	0.00	1.17	1.17	1.91	3.95	5.86
	BkF	0.00	4.34	4.34	0.00	0.26	0.26	0.85	1.80	2.65
	BaP	2.48	23.93	26.41	2.06	13.30	15.36	0.83	11.65	12.48
	DBA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
6-ring	BghiPe	0.00	25.53	25.53	1.70	0.00	1.70	0.00	2.55	2.55
	IDP	0.00	0.00	0.00	0.00	2.60	2.60	0.00	0.00	0.00
	Total (average)	704.08	288.47	992.55	365.69	124.02	489.71	230.50	79.05	309.54
NPAH (ng L^{-1})										
3-ring	2-NF	1.10	0.09	1.19	0.20	0.10	0.30	0.18	0.09	0.26
	FNF	2.86	1.15	4.01	2.35	1.05	3.40	1.95	1.04	2.88
	2-NA	0.05	0.02	0.07	0.01	0.00	0.01	0.01	0.02	0.03
	9-NA	0.09	0.01	0.11	0.01	0.01	0.02	0.01	0.01	0.02
4-ring	3-NBA	1.00	0.81	1.81	0.20	0.40	0.60	0.25	0.31	0.55
	1-NP	0.09	0.12	0.21	0.01	0.03	0.04	0.00	0.01	0.01
	6-NC	0.10	0.37	0.47	0.05	0.07	0.12	0.04	0.08	0.12
	7-NBaA	0.01	0.03	0.04	0.00	0.02	0.02	0.00	0.01	0.01
5-ring	6-NBaP	0.004	0.010	0.01	0.002	0.01	0.01	0.002	0.001	0.00
	Total (average)	5.31	2.61	7.91	2.84	1.78	4.53	2.45	1.69	3.80

Table 2: Comparison of Molecular indices concentration ratios at the examined sites along Alexandria coast

Site	Phe/Ant	Flu/Pyr	[1-NP/Pyr]	[6-NC/Chr]
Alex1	11.4	1.1	3×10^{-3}	3×10^{-2}
Alex2	9.0	1.2	2×10^{-2}	4×10^{-2}
Alex3	8.1	1.9	1×10^{-2}	7×10^{-2}

Phe/Ant (Phe: Phenanthrene, Ant: Anthracene) and Flu/Pyr (Flu: Fluoranthene, Pyr: Pyrene), NP-Nitropolycyclic, nitrochrysene (NC), chrysene (Chr)

In the current study, the highest concentrations were detected at Alex1 which may due to the high inputs of different contaminants to the sea at this site followed by Alex2 and Alex3, respectively.

Composition of (DP and PP) PAHs and NPAHs: The studied characteristics and features of dissolved phase PAHs and NPAHs were significantly different from those for particulate phase. Low molecular weights (LMW) PAHs with two and three aromatic rings like Nap, Ace (MW 128-178) were the predominant compounds in the dissolved phase. These results are compatible with the higher solubility of LMW PAHs. Whereas, the intermediate MW four ring PAHs like Frt and Pyr (MW 202) are considered as highly hydrophobic compounds that found mainly abundant in the PP. This finding is consistent with the obtained results showing a significant amount of Frt and pyr mainly occur in the PP, although they have also a significant concentration among the high MW4-6 ring PAHs in the DP.

For NPAHs, the predominant compounds in both DP and PP are 2-NF, FNF and 3-NBA. These results confirm that high molecular weight (HMW) organic compounds are the predominant contaminants in PP however, LMW organic compounds are the predominant contaminants in DP (Fig. 4a-d).

Source identification: The major PAH and NPAH sources were identified mainly in this study as urban runoff, motor ship maintenance, wastewater discharging, residential and touristic activities. The detected concentration of PAHs and NPAHs found in particular samples mostly reflects the emission sources of such organic compounds[9,13]. PAHs and their derivatives aroused from pyrolytic or petrogenic origin may be used as a characteristic finger print to differentiate between

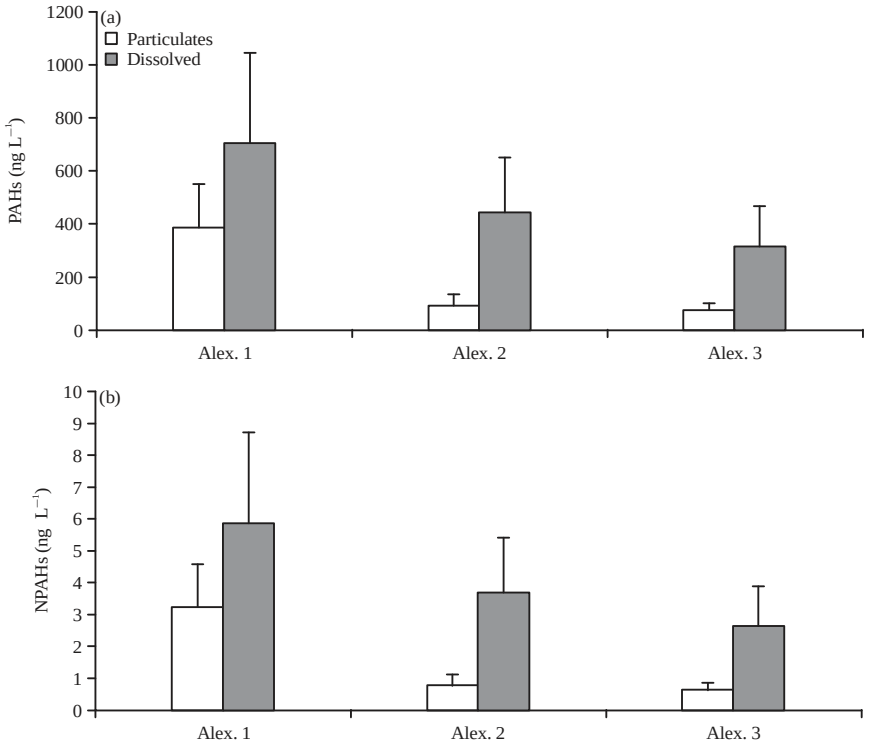

Fig. 2(a-b): Particulate and dissolved PAH and NPAH concentrations of Mediterranean Sea water at different sites along Alexandria coast

Total PAH and NPAH concentrations of Mediterranean Sea water at the investigated sites along Alexandria coast (a) Total PAHs (= Frt+Pyr+BaA+Chr+BbF+BkF+BaP+BghiPe+IDP) and (b) NPAHs (= 2NF+FNF+2-NA +9-NA+3-NBA+1-NB+6-NC+7-NBaA + 6-NbaP) Each column and vertical bar represent mean values and SD, respectively

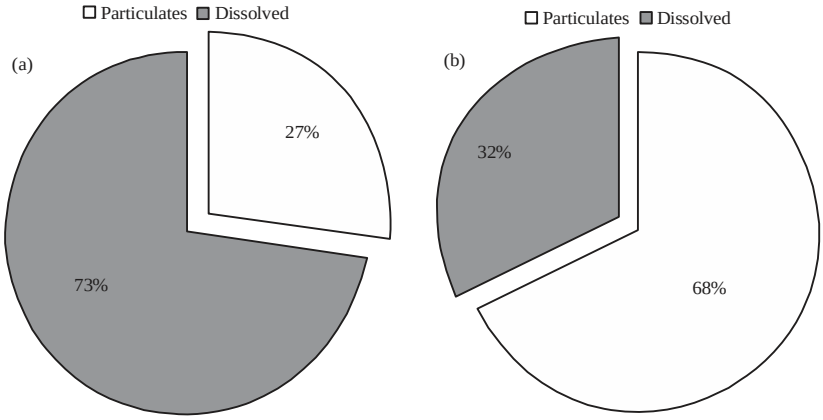

Fig. 3(a-b): Percentage of total Particulate and dissolved PAH concentrations of Mediterranean Sea water at different sites along Alexandria coast

Total PAH and NPAH concentrations of Mediterranean Sea water at the investigated sites along Alexandria coast (a) Total PAHs (= Frt + Pyr + BaA + Chr + BbF+BkF+BaP+BghiPe+IDP) and (b) NPAHs (= 2NF + FNF + 2-NA + 9-NA+3-NBA+1-NB+6-NC+7-NBaA+6-NBaP)

these two origins by using PAH and NPAH molecular indices ratios[8,4,18]. In this study, Table 2 shows water samples collected from sites (Alex2 and Alex3) with Phe/Ant <10 (Phe phenanthrene, Ant anthracene) and Flu/Pyr <1 (Flu fluoranthene, Pyr pyrene) showed strong pyrolytic origin, while water samples collected from site (Alex1) with Phe/Ant >10 and Flu/Pyr<1 were characteristic of a mixed pattern of pyrolytic and petrogenic contamination[9,10,19,20]. The obtained results showed that pyrolytic fingerprint is highly important for indicating the absence or at least less predominance of

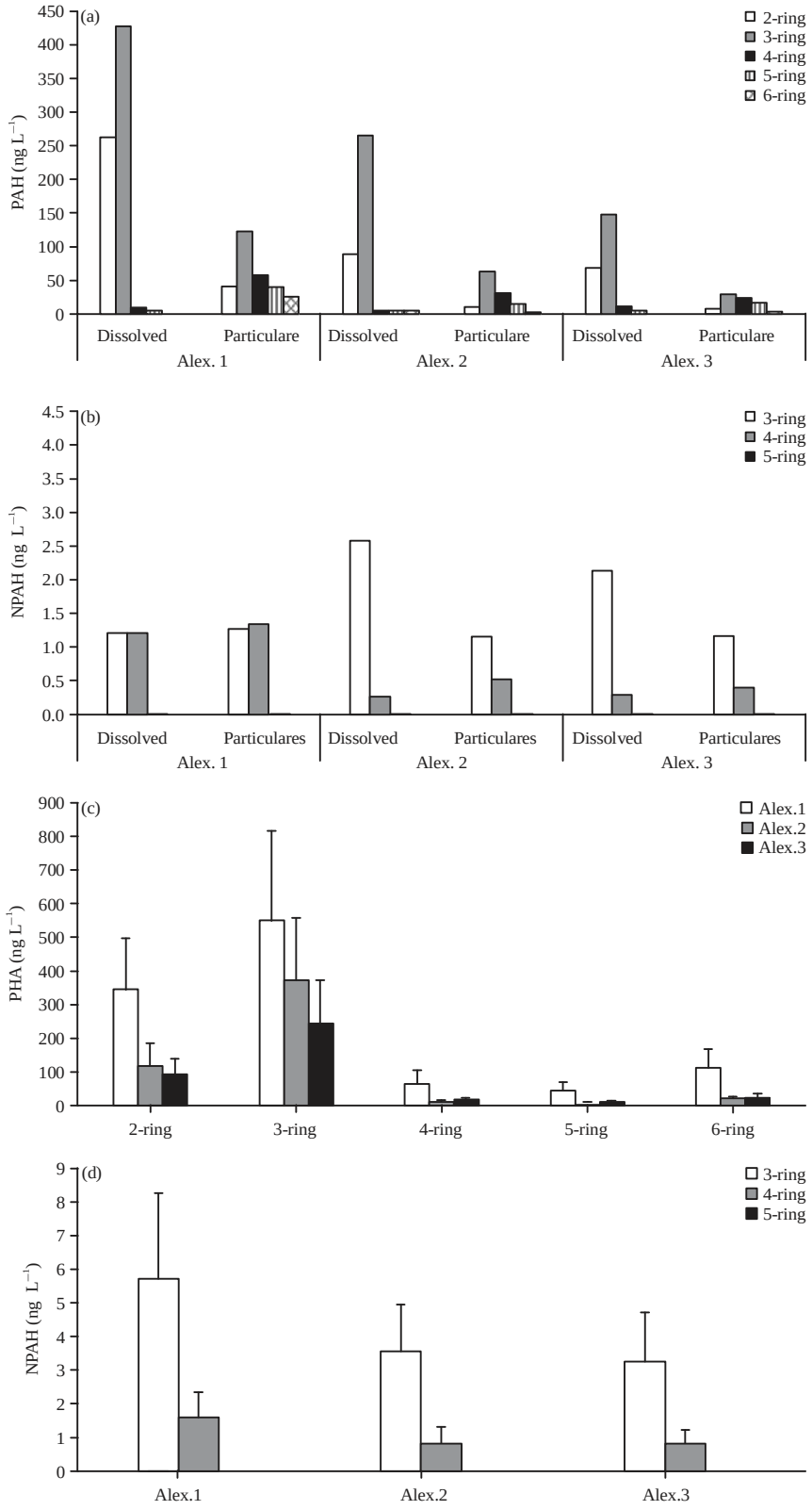

Fig. 4(a-d): Distribution of (2-6 ring) PAH and (3-5 ring) NPAH concentration levels in dissolved and particulate phases of Mediterranean Sea water at the investigated sites along Alexandria coast

Each column and vertical bar represent mean values and SD, respectively

petrogenic origin that cannot be detected in the seawater samples. Therefore, it can be investigated the major abundance of the petrogenic PAHs at the site (Alex1) and pyrogenic sources at (Alex2 and Alex3) sites.

Another important source indicator is the ratio of mono-NPAHs to their parent PAHs. The lower [NPAHs]/ [PAHs] indicating coal exhaust particulate (CEP) emission with lower degree of combustion temperature. Whereas, the higher NPAH/PAH ratio indicating diesel exhaust particulate (DEP) emission with higher degree of temperature. The major contribution of CEP and DEP were estimated from their [1-NP]/[Pyr] and [6-NC]/[Chr] ratios[3,21,22]. This means that the atmospheric [NPAH]/[PAH] ratio widely used to estimate emission sources of PAHs and NPAHs in the atmosphere may be impractical for sea water[9,3,15,16].

This study shows [1-NP]/[Pyr] and [6-NC]/[Chr] ratios were ranged from 0.003-0.01 and 0.03-0.07, respectively, at the three investigated sites, these results indicate a major contributor of the pyrolytic and contamination particularly at sites (Alex2 and Alex3) with a mixed petrogenic pattern from urban runoff inputs and frequent oil spills at site (Alex1).These lower [NPAHs]/[PAHs] values, may due to the high decomposition of NPAHs in sea water by microorganisms.

CONCLUSION

PAHs and NPAHs total concentration levels at the three sampling stations in the Mediterranean Sea along Alexandria coast followed the order: Alex1> Alex2> Alex3. PAHs and NPAHs are mainly predominant in the DP rather than PP. LMW PAHs and NPAHs with two and three aromatic rings are the major fractions in the DP whereas, the HM Ware the major in the PP. The main contributors of such contaminants are mostly derived from petrogenic sources particularly at site Alex1 and from pyrogenic sources at sites (Alex2 and Alex3). We suggest that low [NPAH] / [PAH] ratios may due the high possibility of NPAHs decomposition in sea water by microorganisms.

Overall, NPAHs and PAHs existed in both the dissolved and particulate phase, except for 5 and 6-ring PAHs which only existed in the particulate phase in the sea waters tested. We propose the importance of separating NPAHs in the dissolved and particulate phase when evaluating their concentration levels in sea-water in order to grasp the total extent of pollution. We have to strengthen the environmental laws and policies put in place to control the pollution of all water bodies.

SIGNIFICANCE STATEMENTS

This study was the first one that discussed the dissolved and particulate concentrations and sources of polycyclic aromatic hydrocarbons (PAHs) and their derivatives (NPAHs) in the Mediterranean Sea water along Alexandria coast.

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REFERENCES

1. Lohmann, R., K. Breivik, J. Dachs and D. Muir, 2007. Global fate of POPs: Current and future research directions. Environ. Pollut., 150: 150-165.
2. Parinos, C., A. Gogou, I. Bouloubassi, S. Stavrakakis, E. Plakidi and I. Hatzianestis, 2013. Sources and downward fluxes of polycyclic aromatic hydrocarbons in the open southwestern Black sea. Org. Geochem., 57: 65-75.
3. Nassar, H.F., N. Tang, A. Toriba, F.K. Abdel-Gawad and K. Hayakawa, 2015. Occurrence and risk assessment of polycyclic cyclic aromatic hydrocarbons (PAHs) and their nitrated derivatives (NPAHs) at Nile river and Esmailia canal in Egypt. Int. J. Sci. Eng. Res., 8: 1983-2006.
4. Hong, Q., Y. Wang, X. Luo, S. Chen and J. Chen *et al*., 2012. Occurrence of polychlorinated biphenyls (PCBs) together with sediment properties in the surface sediments of the Bering sea, Chukchi sea and Canada basin. Chemosphere, 88: 1340-1345.
5. Manzetti, S., 2013. Polycyclic aromatic hydrocarbons in the environment: Environmental fate and transformation. Polycyclic Aromatic Compounds, 33: 311-330.
6. Nassar, H.F., T. Kameda, A. Toriba and K. Hayakawa, 2012. Characteristics of Polycyclic Aromatic Hydrocarbons and Selected Nitro Derivatives in Cairo, Egypt from the Comparison with Japanese Typical Traffic and Industrial Cities. In: Proceedings of the 2011 INEF Environmental Forensic Conference, Morrison, R. and G. O'Sullivan (Eds.)., Royal Society of Chemistry, Cambridge, UK., pp: 171-180.
7. Kim, K.H., S.A. Jahan, E. Kabir and R.J. Brown, 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environ. Int., 60: 71-80.
8. Nassar, H.F., N. Tang, A. Toriba, F.K. Abdel-Gawad, G. Guerriero, S.M. Bassem and K. Hayakawa, 2015. Environmental carcinogenic polycyclic aromatic hydrocarbons (PAHs): Concentrations, sources and hazard effects. Int. J. Adv. Res., 10: 511-524.
9. Nassar, H.F., N. Tang, T. Kameda, A. Toriba, M.I. Khoder and K. Hayakawa, 2011. Atmospheric concentrations of polycyclic aromatic hydrocarbons and selected nitrated derivatives in Greater Cairo, Egypt. Atmos. Environ., 45: 7352-7359.

10. Li, Y., S. Yoshida, Y. Chondo, H. Nassar and N. Tang *et al*., 2012. On-line concentration and fluorescence determination HPLC for polycyclic aromatic hydrocarbons in seawater samples and its application to Japan sea. Chem. Pharm. Bull., 60: 531-535.
11. Jurado, E., J.M. Zaldivar, D. Marinov and J. Dachs, 2007. Fate of persistent organic pollutants in the water column: Does turbulent mixing matter? Mar. Pollut. Bull., 54: 441-451.
12. Cai, M., M. Liu, Q. Hong, J. Lin and P. Huang *et al*., 2016. Fate of polycyclic aromatic hydrocarbons in seawater from the Western Pacific to the Southern ocean (17.5°N to 69.2° S) and their inventories on the antarctic shelf. Environ. Sci. Technol., 50: 9161-9168.
13. Brandli, R.C., T.D. Bucheli, T. Kupper, J. Mayer, F.X. Stadelmann and J. Tarradellas, 2007. Fate of PCBs, PAHs and their source characteristic ratios during composting and digestion of source-separated organic waste in full-scale plants. Environ. Pollut., 148: 520-528.
14. Park, S.S., Y.J. Kim and C.H. Kang, 2002. Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. Atmos. Environ., 36: 2917-2924.
15. Tang, N., T. Hattori, R. Taga, K. Igarashi and X. Yang *et al*., 2005. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries. Atmos. Environ., 39: 5817-5826.
16. Hattori, T., N. Tang, K. Tamura, A. Hokoda and X. Yang *et al*., 2007. Particulate polycyclic aromatic hydrocarbons and their nitrated derivatives in three cities in Liaoning province, China. Environ. Forensics, 8: 165-172.
17. Hayakawa, K., F. Makino, M. Yasuma, S. Yoshida and Y. Chondo *et al*., 2016. Polycyclic aromatic hydrocarbons in surface water of the Southeastern Japan sea. Chem. Pharm. Bull., 64: 625-631.
18. Chetwittayachan, T., D. Shimazaki and K. Yamamoto, 2002. A comparison of temporal variation of Particle-bound Polycyclic Aromatic Hydrocarbons (pPAHs) concentration in different urban environments: Tokyo, Japan and Bangkok, Thailand. Atmos. Environ., 36: 2027-2037.
19. Hayakawa, K., Y. Onoda, C. Tachikawa, S. Hosoi and M. Yoshita *et al*., 2007. Estrogenic/antiesterogenic activates of benzo [a] pyrenemonohydroxy derivatives. J. Health Sci., 53: 562-570.
20. Chen, L., Y. Ran, B. Xing, B. Mai and J. He *et al*., 2005. Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China. Chemosphere, 60: 879-890.
21. Bamford, H.A. and J.E. Baker, 2003. Nitro-polycyclic aromatic hydrocarbon concentrations and sources in urban and suburban atmospheres of the Mid-Atlantic region. Atmos. Environ., 37: 2077-2091.
22. Boehm, P.D., K.J. Murray and L.L. Cook, 2016. Distribution and attenuation of polycyclic aromatic hydrocarbons in Gulf of Mexico seawater from the deepwater horizon oil accident. Environ. Sci. Technol., 50: 584-592.