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Polycyclic Aromatic Hydrocarbons analyzed in drinking water collected on four sites in Lebanon

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ABSTRACT
Water pollution by polycyclic aromatic hydrocarbons (PAHs) is one of the most critical problems causing environmental degradation and the human health standards' declination. This is due to the carcinogen, mutagen and toxic characteristic of such hydrocarbons. In this study, the implementation of HPLC, following liquid-liquid extraction, has proven to be a sensitive and a selective analytical method that allows the detection, with UV detector, and the quantification of these compounds in four samples of Lebanese drinking water (Akkar, Tripoli, Kefraya and Beirut).
Keywords: polycyclic aromatic hydrocarbons; extraction methods; drinking water; HPLC.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) constitute a large group of organic pollutants which includes more than 200 chemical compounds. PAHs are built from at least two aromatic rings without any substituents. They are hardly soluble in water and have high affinity for sorption on the surface of solid materials [1, 2]. It is well known, worldwide, that polycyclic aromatic hydrocarbons (PAHs) are one of the most critical environmental contaminants. They are ubiquitous contaminants of great environmental concern whereby 16 unsaturated PAHs are considered possible or probable human carcinogens. PAHs are consequently listed by the US Environmental Protection Agency (EPA) as priority pollutants [3].

PAHs are formed by incomplete combustion of organic matter such as fossil fuels, forest fires, domestic sewages, animal droppings, wood burning, traffic engines and other organic materials that continuously burn [4, 5]. As well, the derivatives from the digenesis of crude oil and organic matter under anoxic conditions are considered amongst the main PAHs sources [6, 7]. PAHs are widely distributed in the atmosphere, water, soils and sediments [8, 9]. Considerable efforts have been devoted to the analysis of PAHs in a variety of environmental samples [10, 11].

Hydrocarbons found in drinking water are due to both natural and anthropogenic inputs, including the digenetic processes taking place within the water pipes, water transport and sedimentation [12]. Due to the carcinogenic properties and persistence of PAHs in the environment; many countries have taken efforts in reducing PAHs emissions. Understanding the contribution of PAHs emission sources is important for proper management of PAHs levels in the environment [13]. This context has created the obligation to monitor water quality especially for human consumption. Thus, PAHs are classified as priority hazardous substances [14, 15]. The European Water Framework Directive mentions that the sum of the concentrations of several PAHs in water for human use must not exceed 100 ng/L. Moreover, the concentration of benzo[a]pyrène is limited to 10 ng/L [16].

High performance liquid chromatography (HPLC), with ultraviolet (UV) detection, is a common practice in the analysis of PAHs. This technique, which involves liquid-liquid extraction and preconcentration of PAHs from drinking water, has proven ideally suitable for the nonvolatile and thermolabile PAHs. [17-19]

In this paper, we report on the chromatographic identification and quantification of the sixteen PAHs listed as US EPA priority pollutants compounds in four samples of Lebanese drinking water.

MATERIAL AND METHODS
Site Description and Sampling
To compare drinking water contamination in different locations, samples were collected at different stations as depicted in the map of Lebanon, Figure 1.

Figure 1. Map showing the sampling locations in Lebanon

Sampling Procedure
Samples were collected, on weekly basis, from the four sites in the period that extended between March and June 2017 using 1-L amber glass bottles. To minimize contamination, all glassware was cleaned with detergent solution, rinsed with distilled water, heated in an oven at 500°C for eight hours to combust traces of organic matter, and finally rinsed with dichloromethane. Sample extraction was performed within 24 h.
Materials and Reagents
All chemicals were purchased from Sigma-Aldrich Chemical Company. Solvents were of the highest grade of purity commercially available and were used without further purification. The PAH mixture solution containing 16 USEPA priority PAHs standard [naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fle), phenanthrene (Phe), anthracene (Anth), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DBA) and benzo[g,h,i]perylene (BgP)], each at 10 µg·mL^{-1} in acetonitrile, was purchased from Sigma-Aldrich. In order to exclude impurities before use, analytical-grade anhydrous Na_2SO_4 was used.
Extraction of PAHs
The general overall method used is described in the literature.[18] The initial 1 L water sample, to be analyzed, was equally divided into two 500 mL fractions. For each fraction, two successive extractions were carried out. Each extraction involved the addition of 100 mL of dichloromethane while letting the mixture shack for one hour with a stirring bar on a magnetic agitator. The mixture was then extracted using a separating funnel. All extracts, combined to a total of 400 mL of dichloromethane, were dried with anhydrous Na_2SO_4, and concentrated by rotary evaporation to a 1 mL residue liquid for HPLC analysis. **Figure 2** summarizes the extraction procedure of PAHs from drinking water.
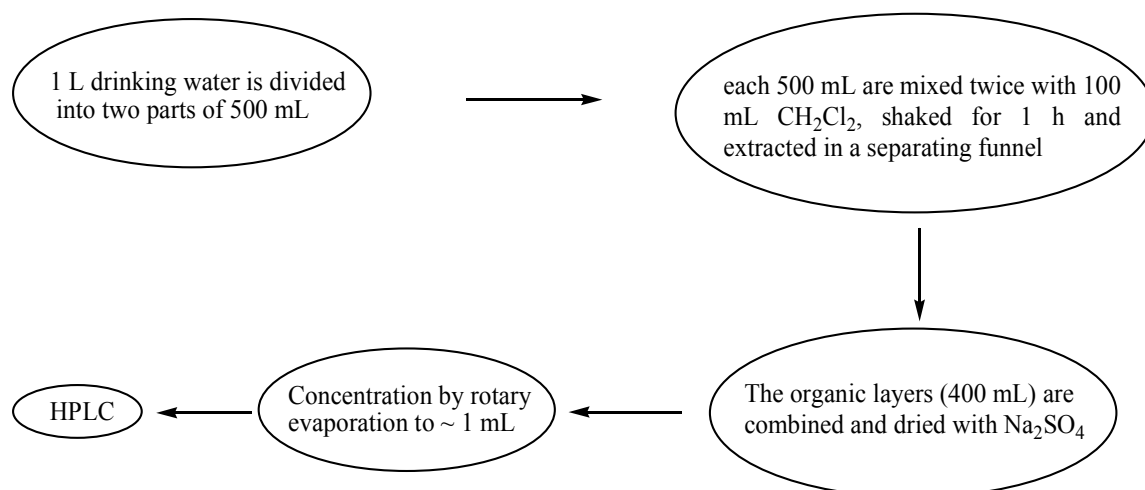
Figure 2. Extraction procedure for the recovery of PAHs from drinking water

Instrumentation
Chromatographic studies were performed on a Schimadzu HPLC system (UFLC) equipped with a thermostated-column device, a degasser and a variable-wavelength UV detector. The column used for analytical HPLC was C-18 (150 mm × 4.6 mm). The mobile phase was a mixture of acetonitrile/water (60/40 %) with a flow rate of 1mL/min. The wavelength of UV detector was set at 254 nm and the column was operated at room temperature. The injection volume was 20 μL.
Dosage of PAHs detected
The second part of the study consists of determining the concentration of each PAHs identified in the samples obtained from the four locations. For this purpose, a series of dilutions of the standard stock solution (2, 4, 6 and 8 μg/mL) was prepared. The corresponding chromatograms recorded clearly showed the variation of the surface of each peak as a function of the concentration prepared.

RESULTS AND DISCUSSION
The retention times of the various PAHs depend on the selected column. For the C-18 column used in our experiments, a total duration of 45 min was needed for the analysis. The first step consisted in passing the 16 USEPA priority PAHs standards in HPLC. The goal of this step was to obtain the chromatogram and, accordingly, the characteristics (retention time) of the various PAHs existing in the standard; as references for further analysis.
The second step was to pass the samples of drinking water, obtained from the four locations, under the same conditions. The presence of several PAHs in these samples, from the various locations, was confirmed by reflecting on the standard, simply by comparing their corresponding chromatograms. The characteristics of the detected PAHs for each location are given in **Table 1**.

Table 1. Characteristics of the PAHs detected in the four drinking water samples

Site	Compound	Retention Time (min)	Area
	Naphtalene	5.7	11520
	Acenaphthylene	6.3	11660
Akkar	Anthracene	12.6	7183
	Fluoranthene	14.5	23266
	Pyrene	15.7	7686
	Naphtalene	5.6	1386
	Acenaphthylene	6.3	36018
	Fluorene	9.9	29710
Tripoli	Anthracene	12.6	6546
	Fluoranthene	14.3	1440
	Pyrene	15.9	1713
	Chrysene	21.7	69119

	Naphtalene	5.8	10548
Kefraya	Acenaphtylene	6.2	3214
	Fluoranthene	14.5	2219
	Naphtalene	5.6	105830
Beirut	Acenaphtene	7.8	160452
	Benzo(a)anthracene	19.9	963

In the third step of the study, the concentration of each PAH, as detected in the different locations, was calculated. The method used is based on the graphical representation of curves, obtained by means of the experimental measurements using Origin 6.0 professional program. The results are summarized in Table 2.

As shown in Table 1, a total of nine (9) PAHs were detected in the different four locations. Seven (7) of these PAHs were detected in Tripoli; an indication of the bad quality of drinking water in comparison to the other three locations. Naphtalene was the only PAH which was commonly present in the four locations, while Acenaphtylene and Fluoranthene were detected in the three locations: Akkar, Tripoli and Kefraya. Anthracene and Pyrene were detected for Akkar and Tripoli, whereas, Fluorene and Chrysene were detected only in Tripoli. In Beirut, on the other hand, no PAHs were detected in common with any of the other three locations except for Naphtalene, as mentioned above. Instead two new PAHs: Acenaphtene and Benzo(a)anthracene were detected.

The results from Table 2 showed that the total PAHs concentrations (ΣPAHs) range from 8235 to 26260 ng/L. The highest PAH levels were found in the samples collected from Beirut followed by those of the samples obtained from Tripoli. The ΣPAHs levels were higher in the samples collected from the urban sites (Tripoli and Beirut) and lower in samples collected from the rural sites (Akkar and Kefraya). The total PAH concentrations recorded in this study are comparable to some values reported in literature.[3] It can, therefore, be deduced that the increase of PAH concentrations in urban sites reflects higher input of anthropogenic PAHs. The same conclusion could be reached to by comparing the PAHs detected in the drinking water in Beirut (a much bigger city with more industry and heavier traffic conditions) versus those detected for Tripoli (a smaller and a less populated city known, till only a few years back, by its extended orange orchards and green areas) and their concentrations. The sum of the seven PAHs levels detected in Tripoli is only 12290 ng/L compared to the 26260 ng/L detected for the three PAHs found in Beirut. As a matter of fact, the Level of Naphtalene detected in Beirut was found to be higher than the sum of levels of all seven PAHs found in Tripoli combined. It is obvious; therefore, that the composition and concentration of the different PAHs varies in the different regions based on climate, geographical location, topographic relief, and the activities that take place. In this respect, it is worthwhile mentioning that the five (5) PAHs detected in Akkar are all detected in Tripoli and at comparable concentrations. Despite the fact that Tripoli is a city and Akkar is a rural area, both locations receive their drinking water from springs and rivers originating from the same mountain chain that surrounds and overlooks the two areas. The relatively low concentrations, indicate that the sources of such PAHs are mainly due to natural processes.

Table 2. Concentration of PAHs detected in the four water samples in ng/L

| HAP Detected	Concentration in water of Akkar (ng/L)	Concentration in water of Tripoli (ng/L)	Concentration in water of Kefraya (ng/L)	Concentration in water of Beirut (ng/L)
Naphtalene	2715	1320	2430	16500
Acenaphtylene	1120	2820	5200	-
Fluorene	-	2310	-	-
Anthracene	1250	1130	-	-
Fluoranthene	1520	1110	1250	-
Acenaphtene	-	-	-	8330
Pyrene	1630	1340	-	-
Chrysene	-	2260	-	-
Benz(a)anthracene	-	-	-	1430
ΣPAHs	8235	12290	8880	26260

The relative contribution of each individual PAH to the total PAH concentration has been determined for the four sampling sites and are presented in **Figure 3**.
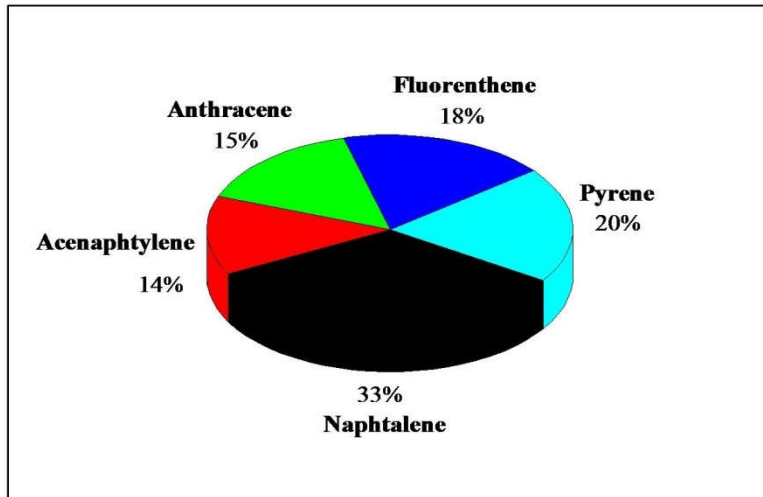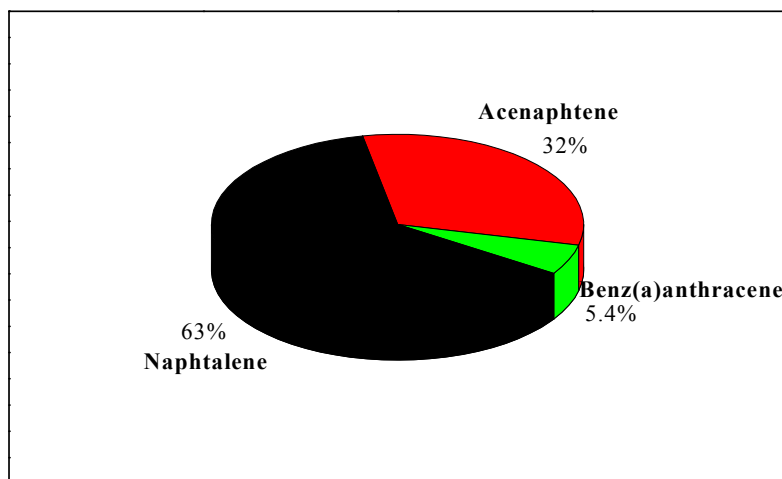
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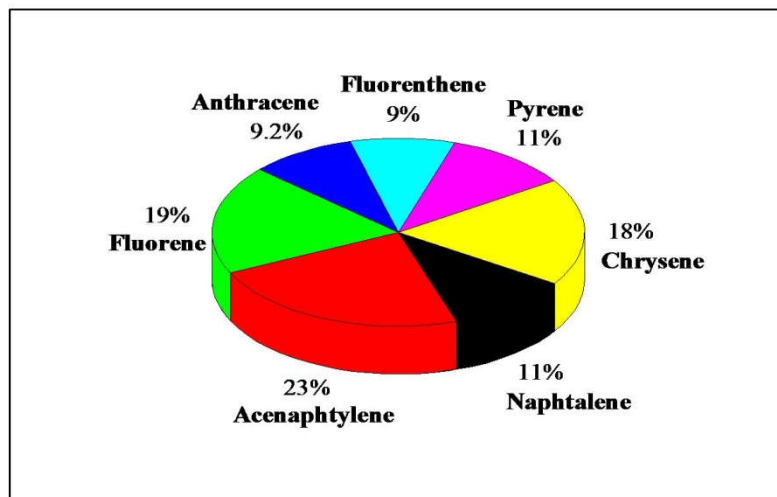
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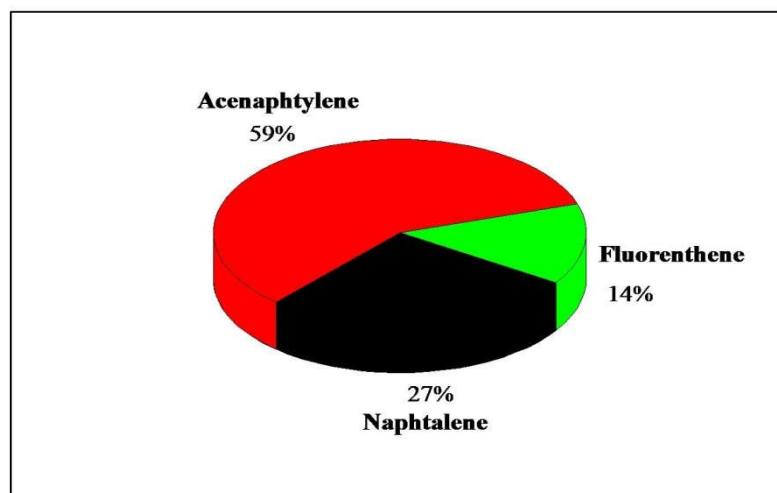
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Figure 3. Contribution of each individual PAH to the total PAHs in drinking water analyzed at a) Akkar, b) Tripoli, c) Kefraya and d) Beirut

Water samples from the four areas exhibit similar PAH patterns, with a predominance of two- three-ring PAH compounds. The results obtained show high PAHs contaminations in the drinking water of all samples. This, therefore, calls for effective water treatment and efficient purification in order to get rid of any present contamination.

Reproducibility
The reproducibility of the methods has been determined by replicate analysis of three separate samples in addition of the working standard. The results have proven satisfactory with relative
standard deviations not exceeding 2% and the correlation coefficients (*r*) were greater than 0.999 for all the analyzed compounds.

CONCLUSION
Polycyclic aromatic hydrocarbons (PAHs) constitute a large group of organic contaminants. These compounds usually are in the form of mixtures, their main sources are the human activities. PAHs are low soluble in water. The presence of large amounts of PAHs in drinking water is associated with numerous problems including the high toxicity to living organisms, including humans. Prolonged exposure to PAHs, on the other hand, contributes also to the induction of spontaneous genetic changes which may lead to carcinogenesis. The results presented clearly indicate that the effective monitoring of PAHs content is a matter of high priority for human and environmental safety as well.
The basic technique used for the quantitative isolation of PAHs from water is the liquid-liquid extraction method. Good resolution was achieved in a single run on a C18 column using 60/40 mixture of acetonitrile-water as the mobile phase, while spectrophotometric detection at optimized wavelength is used.
The objective of this work was the identification and quantification of polycyclic aromatic hydrocarbons in different drinking water samples (Akkar, Tripoli, Kefraya and Beirut). In the first part of this work, we extracted PAHs from each water sample analyzed, and then a study on HPLC was carried out. A standard of 16 commercial PAHs allowed us, by a simple comparison, to confirm the presence of five PAHs in Akkar water (Naphtalene, Acenaphthylene, Anthracene, Fluoranthene and Pyrene), 7 PAHs in Tripoli water (Naphtalene, Acenaphthylene, Fluorene, Anthracene, Fluoranthene, Pyrene and Chrysene), 3 PAHs in Kefraya water (naphthalene, acenaphthylene and fluoranthene) and 3 PAHs in Beirut water (naphthalene, acenaphthene and benz(a)anthracene).
In the second part of this work we determined the concentration of each PAH detected in each of the four analyzed samples. We followed the standard calibration method. The precision is quiet satisfactory.

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