Field Validation of Polyethylene Passive Air Samplers for Parent and Alkylated PAHs in Alexandria, Egypt

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ABSTRACT: Polyethylene samplers (PEs) were deployed at 11 locations in Alexandria, Egypt during summer and winter to test and characterize them as passive samplers for concentrations, sources, and seasonal variations of atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs). PE–air equilibrium was attained faster for a wider range of PAHs during the winter season possibly due to increased wind speeds. Calculated PE–air partitioning constants, $K_{PE,A}$, in our study [Log $K_{PE,A} = 0.9426 \times \text{Log} K_{OA} - 0.022$ ($n = 12, R^2 = 0.99, \text{Std error} = 0.053$)] agreed with literature values within <46%. For parent (except naphthalene), mono- and dialkylated PAHs, active sampling based concentrations of PAHs were within an average factor of 1.4 (1.0–5.6) compared to the PE based values. For C3+ alkylated PAHs, $K_{PE,A}$ values were lower than predicted, on average by ~0.8 log units per carbon in the alklylation. Enthalpies of vaporization ($\Delta H_{vap}$) accurately corrected $K_{PE,A}$ for temperature differences between winter and summer sampling. PAH profiles were dominated by naphthalene, phenanthrene, and alkylated phenanthrenes. Calculated diagnostic ratios indicated that PAHs originated mainly from vehicle emissions.

INTRODUCTION

Urban air pollution is of major concern in Egypt as industrial wastes, traffic congestion, and overcrowding in cities release pollutants that greatly contribute to environmental damage.1 Polycyclic aromatic hydrocarbons (PAHs) are a group of organic pollutants that are present in the atmosphere due to emissions from gasoline- and diesel-powered vehicles,2 municipal and commercial incinerators,3 residential heating systems that combust fuels such as coal, wood, gas, and oil, various industrial processes, and volatilization from polluted grounds.4 The main concern of PAHs is that some have carcinogenic properties that are associated with increasing size of the molecule (4–6 rings) and their metabolic transformation to reactive diol epoxides.

Despite the importance of the atmospheric pathway for human exposure, atmospheric monitoring of PAHs is not routinely performed in Egypt. This is mainly due to the requirements of expensive high-volume sampling equipment, which is reliant on continuous field maintenance and electricity to operate. Thus the availability of data regarding atmospheric PAH concentrations is sparse5,6 or lacking. In Alexandria for example, eight monitoring stations were established for monitoring the atmospheric quality since the establishment of the Egyptian environmental Law (Law No. 4, 1994). These monitoring stations previously were used to continuously collect data on the levels of some gases ($\text{NO}_x$, $\text{SO}_2$, $\text{CO}$, $\text{O}_3$) and particulates (TSP and PM$_{10}$) (see text SI 1, Figures SI 1 and SI 2 for more details). To our knowledge, most of these stations are not operating at the moment. The lack of data has posed some difficulties for establishing pollution control and management plans. Cheap and easy air sampling techniques are therefore helpful or sometimes the only choice for surveys.

Passive air samplers have proven to be a powerful monitoring technique for SOCs, and they are cheaper and require less labor compared to active samplers7–13 (Table SI 1). By using passive samplers, more measurements can be undertaken to establish spatial and temporal trends at reduced cost. Yet many substances measured with passive sampling do not reach equilibrium during the exposure period. This is a drawback to some extent because it makes the in situ calibration of the uptake process necessary which is associated with a degree of uncertainty. However, the major advantage is that a time-integrated concentration is obtained that can be used for compliance checking with time-averaged standards. Because of the long exposure periods of passive samplers, the exact size and timing of a peak concentration cannot be specified, making it less suitable for compliance checking with the maximum acceptable concentration. One important drawback of passive samplers is that if a sample is lost, it is not possible to collect a new sample quickly. This is due to the required exposure time.© 2012 American Chemical Society

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Active sampling has advantages as an established and accepted method for determining atmospheric concentrations of pollutants both in the gas and particulate phases. The preferential occurrence of a chemical pollutant in the gaseous phase or the particulate phase will greatly depend on the prevailing environmental factors and the physicochemical properties of the chemical pollutant. Most of the lower molecular weight PAHs (2–3 rings PAHs), for example, will occur in the gaseous phase compared to the higher molecular weight PAHs (5–6 rings PAHs) which are mainly associated with the airborne particles. Thus in risk assessment studies, passive sampling of PAHs will be less suitable as most of the PAHs classified as toxic or carcinogenic (5–6 rings PAHs) will occur in the particulate phase. However, the applications of active samplers in monitoring studies also encounter limitations and disadvantages (Table SI 1). Active samplers are noisy (an issue in residential environments), need electricity (a problem in remote areas where energy supplies may be lacking), and are expensive since pumps are costly, labor intensive, and time-consuming. These are reasons for low temporal and spatial resolution in many monitoring networks. Moreover, other possible artifacts of active samplers are breakthrough of pollutants and degassing of pollutants from particles on the filter which both affect the quality of the measurement.4,15

We suggest that passive samplers are the best option for determining background concentrations of semivolatile organic compounds in places were no data exist. Depending on the obtained results, decision makers could decide which places requires more detailed investigation (applying the conventional active samplers) and which locations can be skipped (when detected concentrations are below quality standard standards). Once it has been determined several times with passive sampling that concentrations are well below the standard, the sampling frequency may be reduced, thereby saving costs.

The basic theory underlying the accumulation of SOCs in passive air samplers via diffusion and absorption into the sampler matrix has been detailed previously.16 Low-density polyethylene (LDPE) has been successfully used as passive samplers in sediments’ porewater,17–19 the water column,20–22 and atmosphere,23,24 as well as to as assess the activity gradients across sediment–water20 and water–air interfaces.21

The atmospheric pollution problem in Egypt1 caused by unrestricted atmospheric emissions not only creates serious health hazards but also travels over long distances, causing deterioration of ambient air quality.26 This encouraged us to investigate the possibility of using LDPE as passive air samplers for PAHs in the atmospheric environment of Alexandria, Egypt. Accordingly, we undertook two major 21-day sampling campaigns of 15 deployments each during summer (July 2010) and winter (January 2011) across 11 sites to (i) test and characterize LDPEs as passive samplers for measuring expected elevated concentrations of gaseous PAHs in the ambient air of Alexandria; (ii) determine uptake kinetics and equilibration times for PAHs in the LDPE; (iii) evaluate PE-based concentrations compared to those from simultaneously performed active high-volume sampling; (iv) establish baseline concentrations of gaseous PAHs and investigate their spatial and temporal variations; and (v) determine the main sources of PAHs in Alexandria.

## MATERIALS AND METHODS

### Site Description

Alexandria is the second-largest city of Egypt, with a total surface area of 2300 km² and a population of 4.1 million, extending about 90 km along the coast of the Mediterranean Sea on the northwestern side of the Nile Delta (Figure SI 3).27 It is Egypt’s largest seaport, serving approximately 80% of Egypt’s imports and exports. Forty percent of the industrial activities and 60% of the petroleum activities of Egypt are concentrated in Alexandria.27 As a seaside city, it is an important tourist and recreational resort receiving about 2 million tourists every year. Alexandria has an arid climate, but the prevailing north wind, blowing across the Mediterranean, gives the city a climate different from the desert hinterland. The city’s climate shows Mediterranean characteristics, namely mild, variably rainy winters and hot summers that, at times, can be very humid; January and February are the coolest months, with daily maximum temperatures typically ranging from 12 to 18 °C and minimum temperatures that could reach 5 °C. Alexandria experiences violent storms, rain, and sometimes hail during the cooler months. July and August are the hottest and driest months of the year, with an average daily maximum temperature of 30 °C.27

### High-Volume and PE Samplers Preparation

PEs were cut from commercial sheeting (Carlisle Plastics, Inc., Minneapolis, MN) with a thickness of 51 μm, yielding a 10 × 30 cm strip of ~1–2 g each. PEs were precleaned twice in dichloromethane (DCM) and n-hexane for 24 h respectively. After precleaning, 12–14 PEs were immersed in an 80:20 (v/v) methanol/water solution spiked with performance reference compounds (PRCs) at a nominal concentration of 5 μg per sample in methanol for 30 days.28 Three deuterated PAHs were selected to serve as PRCs (for more details see Text SI 2). Once spiked, PEs were strung on stainless steel wires, placed in precleaned aluminum foil packets, numbered, and frozen until the time of deployment. Polyurethane foam (PUF, Tisch Environmental, Cleves, OH) plugs for the codeployed active samplers were Soxhlet extracted with DCM for 48 h. Glass fiber filters (GFF, Whatman, Piscataway, NJ) were combusted overnight in an oven at 450 °C. All samplers (including field blanks) were wrapped in solvent-rinsed aluminum foil immediately after preparation and stored until the time of sampling.

### Deployment of PEs

PEs were deployed ~2 m above the ground surface in 11 different locations across Alexandria city (Figure SI 3) each inside two inverted bowls providing protection from direct radiation and rainfall. At each location, PEs were deployed for 21 days in July 2010 (summer season) and January 2011 (winter season). Deployment locations were carefully selected to represent different activities including residential, traffic, industrial, and mixed activities (Site and deployment details are given in Table SI 2). At one of the sites (St 11), three PEs were deployed simultaneously in separate bowls (during both seasons) and one was retrieved every week to determine uptake kinetics and equilibration times for PAHs.

### Active Air Sampling

Twenty-two atmospheric samples were collected using a high-volume sampler at the 11 sites in July 2010 and January 2011 (for meteorological details and sampling volumes, see Text SI 3 and Table SI 3). Air was first drawn through a GFF to collect the particulate-bound compounds followed by a PUF to retain the vapor-phase compounds. Particulate-bound PAH data are not presented in the current study.

### Extraction of PEs and PUFs

The method employed for extraction of PEs has been described elsewhere.27 Briefly, PEs were cleaned and cold extracted twice in DCM for 24 h after spiking with 10 μL of a surrogate standard mixture composed

of deuterated PAHs (d_{10}-acenaphthene, d_{10}B-phenanthrene, d_{12}B-chrysene, and d_{12}B-pyrene; 5 ng/μL in nonane). Extracts were combined at the end of the extraction period and concentrated to ~1 mL on a rotary evaporator, solvent-exchanged to hexane, and concentrated to ~50 μL. Ten μL of d_{14}B-terphenyl (10 ng/μL) was added as an injection standard before analysis.

PUF samples were extracted using a Dionex ASE 350 (Dionex Corporation, Sunnyvale, CA) accelerated solvent extraction device after spiking with the surrogate standard mixture. n-Hexane/acetone (3:1) was used as the extraction solvent mixture. Extracts were concentrated to a final volume of ~1 mL using a rotary evaporator (after solvent exchange into hexane) and passed on a glass chromatographic cleanup column packed with silica gel/alumina in order to remove the interfering compounds. PAHs were eluted with n-hexane/DCM solvent mixture and the collected fraction was concentrated to a final volume of ~50 μL. Finally, d_{14}B-terphenyl was added as the injection standard before analysis (see Text SI 4 for more details).

Instrumental Analysis and Quality Control. PAHs were analyzed with an Agilent 6890 Series GC System connected to an Agilent 5973 Network Mass Selective Detector. Separation of PAHs was accomplished with a DB-5 MS fused silica capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific). Samples (1 μL) were auto injected in splitless mode with the injection port at 275 °C. The MS was operated in EI+ mode with selected ion monitoring. Samples were analyzed for 42 PAHs (details are given in Text SI 5 and Table SI 4).

Overall, the analysis included procedural blanks, field blanks, matrix spikes, and duplicate samples, which were carried throughout the entire analytical procedure in a manner identical to the samples. Limits of detection (LODs) were derived from the blanks and quantified as three times the standard deviation of the mean concentration in the blanks. When individual PAHs were not detected in blanks (as the case of 5–6 rings PAHs in the PUF samples), LODs were calculated as the mean value of the baseline noise plus three times the standard deviation of this noise (QA/QC procedures are detailed in Text SI 6 and Table SI 4).

Physico-Chemical Properties and Temperature-Related Adjustments. To calculate gas-phase concentrations of PAHs from PE passive samplers, a set of partitioning coefficients is required including octanol–air partitioning coefficients (K_{OA}) and sampler–air partitioning coefficient (K_{PE,A}), which are not available for all the individual PAHs investigated in the present study. To derive values for all PAHs, internally consistent K_{OA} coefficients were obtained from Ma et al.30 Available K_{OA} values were correlated against molecular weights to derive K_{OA} values for all PAHs. Results for the individual PAHs which approached equilibrium at St 11 (see Deployment of PEs) were used to derive K_{PE,A} using the following equation:

\[ K_{PE,A} = \frac{C_{PE}}{C_A} \]  

(1)

where \( C_{PE} \) and \( C_A \) are the PAH concentrations in the PE sampler (ng/m³) and the corresponding vapor phase atmospheric concentration of the PAH (ng/m³) obtained from the active sampling. K_{PE,A} for all PAHs were then derived based on a correlation with K_{OA} (Figure SI 4a and b). K_{PE,A} derived here were also compared to those reported by Bartkow et al.23 (see Table SI 5).

\[ K_{PE,A}(T_2) = K_{PE,A}(T_1) \times e^{-\frac{\Delta H_{vap}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)} \]  

(2)

where \( T_2 \) and \( T_1 \) are the mean temperatures of the deployment and at which the partitioning properties were determined (K), \( R \) is the ideal gas constant (J mol⁻¹ K⁻¹), and \( \Delta H_{vap} \) is the enthalpy of vaporization (kJ mol⁻¹). Available \( \Delta H_{vap} \) for PAHs (from ref 31) were correlated against the subcooled liquid vapor pressure (P_L/Pa) (Figure SI 5) obtained from Ma et al.30 to temperature-adjust K_{PE,A} values for all investigated PAHs (Table SI 5).

RESULTS AND DISCUSSION

Accumulation of PAHs in the PE Samplers. Accumulated amounts of PAHs in the PE samplers are summarized in Tables SI 6 and 7. \( \sum \)PAHs ranged from \( 23 \times 10^3 \) to \( 77 \times 10^3 \) ng/g PE in the summer season and from \( 5.7 \times 10^3 \) to \( 60 \times 10^3 \) ng/g PE in the winter season. Concentrations of PAHs accumulated by the PEs were typically higher in the summer season by a factor of ~2. PAH profiles were generally dominated by 2–3 rings PAHs (Figure 1A and B) which represented 74–97% of the total quantified PAHs followed by 4-ring PAHs, indicating that PEs sampled PAHs in the gaseous phase. The most abundant PAHs quantified in both seasons were alkylnaphthalenes and alkylated dibenzothiophenes comprising 42–72% and 11–41%, respectively, of the total quantified amounts of PAHs, followed by fluoranthene (1.2–13%) and pyrene (0.65–9.1%). Phenanthrene was the dominant PAH quantified in passive samplers (PEs, PUF disks, and ethylene vinyl acetate) deployed in Australia,32,33 Europe,34 and Canada.35 All of these studies concentrated mainly on the parent PAHs and alkylated PAHs were not analyzed.
Characterization of Uptake Kinetics and PAH Equilibrium.

The addition of performance reference compounds (PRCs) to the samplers before deployment is useful to infer the exchange rate kinetics, assuming that the elimination rates (of PRCs) and uptake rates (of native compounds) are equivalent. Exchange kinetics are quantified by the elimination or clearance rate constant ($k_e$) (for details, see Text SI 7 and Table SI 8).

The least dissipated PRC was $d_{12}$-benzo(a)pyrene with a higher elimination rate during the winter (52–82%) compared to the summer (25–51%). Calculated clearance rate constants (Table SI 8) of the PRCs were used to determine the % equilibrium of all the accumulated PAHs in the samplers (Tables SI 9 and 10). Based on the PRC loss rates, PAHs up to pyrene ($\log K_{PE-A} = 8.3$) were at or close to equilibrium during the winter season.

Figure 2. Predicted % equilibrium based on calculated $k_e$ values as a function of time (weeks) for PAHs during the summer (A) and winter (B) seasons at site 11 compared to the accumulated amounts of PAHs in the PE samplers (ng/g PE) at each week (A1–3, B1–3).
the summer season, only PAHs up to fluorene reached equilibrium ($\log K_{PE-A} = 6.4$). The lower dissipation rates of $d_{12}$-benz(a)anthracene and $d_{12}$-benzo(a)pyrene in PEs deployed during July 2010 (summer) are probably related to the lower wind speed during the summer season.

Chemical exchange between the surrounding air and the passive sampler is limited by the mass transfer through the air-side boundary layer and/or the sampler membrane. If the chemical exchange is limited by the sampler membrane, then the clearance rate constants, whereas if the chemical exchange is limited by the air-side resistance, then the clearance rate constants, respectively). The lower dissipation rates of PAHs in PEs deployed during July 2010 (summer) are probably related to the lower wind speed during the summer season.

Comparison of Predicted and Observed % Equilibration during Field Deployments. In the present study, three PEs were deployed simultaneously for 1, 2, and 3 weeks each at site 11 during each season. This was done to better understand the equilibration of PAHs in the PEs over time and validate PRC-based equilibration times. Results indicated that % equilibrium between samplers and the surrounding air generally decreased with increasing log $K_{PE-A}$ (Figure 2A and B). Lower molecular weight PAHs attained equilibrium faster than higher molecular weight PAHs. Three different regimes could be observed for the accumulated PAHs in the codeployed PEs. In the first regime, PAHs in PEs were close to or reached equilibrium with the ambient concentration within one week of deployment. This pattern was typical for the lower molecular weight PAHs ($\log K_{PE-A} < 8.1$), but a slight seasonal variation was observed in this group. During the summer season (Figure 2A1), this pattern was observed for PAHs up to C$_2$-naphthalene ($\log K_{PE-A} = 6.1$), whereas in the winter season (Figure 2B1), this pattern extended up to C$_2$-fluorene ($\log K_{PE-A} = 8.0$). In the second regime, PAHs were in the curvelinear phase after a deployment period of three weeks. This pattern was characteristic for PAHs up to C$_2$-phenanthrene/anthracene ($\log K_{PE-A} = 8.6$) in the summer season (Figure 2A2) and perylene ($\log K_{PE-A} = 10.7$) in the winter season (Figure 2B2). In the final regime, PAHs were still in the linear uptake phase after the whole deployment period. This pattern was observed for PAHs with $K_{PE-A} > 8.6$ in the summer season and $K_{PE-A} > 10.7$ in the winter season (Figure 2A3 and 2B3). Overall, there was good agreement between PRC-based equilibration predictions and those observed from the 1-, 2-, and 3-week uptake experiments.

Deriving $K_{PE-A}$ and Their Temperature Adjustment. After characterizing the stage of uptake for each of the target compounds, atmospheric concentrations measured with the codelployed high-volume air sampler were used to estimate $K_{PE-A}$ values for compounds that reached equilibrium. We used concentrations of PAHs that attained equilibrium after 1 week deployment period (Figure 2A1 and 2B1). Calculated $K_{PE-A}$ values (Table SI 5) were correlated against Log $K_{OA}$ and the following equations were obtained (Figure SI 4A, B):

$$\log K_{PE-A}^\text{(summer)} = 0.9142 \times \log K_{OA} + 0.1097$$

($R^2 = 0.993, n = 7, SE = 0.043, SE$ of intercept $= 0.163, SE$ of slope $= 0.024$)

$$\log K_{PE-A}^\text{(winter)} = 0.9711 \times \log K_{OA} - 0.1536$$

($R^2 = 0.975, n = 12, SE = 0.088, SE$ of intercept $= 0.334, SE$ of slope $= 0.049$)

Figure 3. Comparison between predicted and directly measured concentrations of PAHs using $\Delta H_vap$ and $\Delta U_{OA}$ for temperature corrections.
Results from both deployments were averaged to calculate $K_{\text{PE-A}}$ for all the other investigated PAHs according to the following equation:

$$\log K_{\text{PE-A}} = 0.9426 \times \log K_{\text{OA}} - 0.022$$  \hspace{1cm} (5)

($R^2 = 0.991$, $n = 12$, $SE = 0.052$, $SE$ of intercept $= 0.197$, $SE$ of slope $= 0.029$)

Calculated $K_{\text{PE-A}}$ values based on eq 5 were compared with those calculated according to Bartkow et al., Kennedy et al., and Lohmann (Figure SI 6). Our $K_{\text{PE-A}}$ values were in very good agreement with those obtained according to the equation proposed by Bartkow et al. with factor different less than 46% in all the investigated individual PAHs (Table SI 5), and similar to the prediction by Lohmann based on the partitioning of PAHs between PE and water.

Calculated $K_{\text{PE-A}}$ values in our study were temperature corrected using $\Delta H_{\text{vap}}$. The excellent agreement between eqs 3 and 4 (no statistical significant difference between the regression coefficients at $p = 0.001$) indicated that the use of $\Delta H_{\text{vap}}$ accurately corrected $K_{\text{PE-A}}$ for PAHs. In other words the enthalpy of PE–air partitioning ($\Delta H_{\text{PE-A}}$) was dominated by changes in the PAH’s vapor pressure, not by changes in the PE uptake. As an alternative, we also temperature adjusted $K_{\text{PE-A}}$ with the energy of octanol–air exchange ($\Delta U_{\text{OA}}$, kJ/mol) from Beyer et al. and compared it to the correction using $\Delta H_{\text{vap}}$.

Good match (Figure SI 7) between calculated $K_{\text{PE-A}}$ corrected using both enthalpies was observed with a factor difference <55%. For further comparison, we used both enthalpies to correct for temperature differences at one of the sampling locations (St 11) and predicted the vapor-phase concentration of PAHs. As shown in Figure 3, better match (based on the best fit equation) between predicted and directly measured atmospheric concentrations of PAHs was achieved when $\Delta H_{\text{vap}}$ was used for temperature corrections.

**Evaluation of the Predictive Ability of PE Samplers.**

Estimated gaseous concentrations of PAHs calculated from concentrations measured in the PE samplers corrected for nonequilibrium (see Text SI 8) were compared with the gaseous concentrations actually measured in the atmosphere using the high-volume sampler. Results are given in Tables SI 11 and 12. Good agreement was generally observed between PE-derived atmospheric concentrations of PAHs and those obtained from the conventional active sampling in all the investigated samples (Figure 4A, B) during the summer and winter seasons. For parent (except naphthalene), mono- and dialkylated PAHs, active sampling based concentrations of PAHs were within an average factor of 1.4 (1.0–5.6) compared to the PE-based values (Tables SI 11 and 12); for tri- and tetra-alkylated PAHs it was 3.5 (1.0–22). PE-based naphthalene concentrations were up to 9.0 times higher than those obtained from the active sampling, which could be attributed to the lower recovery efficiency and storage capability for naphthalene in the PUFs. In contrast to PE samplers, 5–6 rings PAHs were not quantified in the active air suggesting that, although these compounds were present in the atmosphere, an insufficient volume of air was sampled by the active systems to attain detection limits. At the same time, higher molecular weight PAHs are predominantly found on aerosol particles and only negligible fractions are in the gas phase. Our results indicated that the higher factor differences were observed for tri- and tetra-alkylated dibenzothiophenes and phenanthrenes. We note that the difference in the sampling periods between the passive (21 days) and active (2–3 days) samplers adds uncertainty affecting the degree of agreement between results obtained from both sampling techniques. The good correlations obtained here suggest gas-phase PAH concentrations in Alexandria might not display strong short-term variations during our measurement periods. Overall, PEs have proven to be a powerful tool for predicting atmospheric concentrations of gaseous-phase PAHs in the present study with a higher level of uncertainty for naphthalene and higher alkylated PAHs (C3- and C4-PAHs).

**Uncertainty Analysis of $K_{\text{PE-A}}$ Driven Values for Alkylated PAHs.** Due to the greater difference found between PE-driven and active sampling concentrations of tri- and tetra-alkylated dibenzothiophenes and phenanthrenes, we quantified the uncertainty associated with their predicted $K_{\text{PE-A}}$ values. As mentioned above, the best agreement was observed for parent, mono- and dialkylated PAHs. A regression curve was constructed between active sampling and PE-driven concentrations of PAHs in all the investigated samples during the summer (Figure SI 8A) and winter (Figure SI 8B) seasons. In each season, PAHs were divided into three groups: I (parent, mono- and dialkylated PAHs), II (trialkylated PAHs), and III (tetraalkylated PAHs), and each group was represented by a regression line. The curves showed the deviation in the tri- and tetra-alkylated PAHs as compared to the curve representing the parent, mono- and dialkylated PAHs, which was chosen to represent the optimal model representing the relation between both types of measures. PE-driven concentrations of tri- and tetra-alkylated dibenzothiophenes and phenanthrenes were then recalculated based on the best fit of the optimal model. According to this approach, field-calibrated $K_{\text{PE-A}}$ for alkylated...
PAHs were derived. Field-calibrated $K_{PE,A}$ showed a decrease that ranged from 0.3 to 1.7 log units from the predicted ones (eq 5) resulting in an uncertainty ranging from 31 to 96% in the PE-based concentrations of C$_17$ and C$_{26}$-dibenzoanthiyphenes and phenanthrenes. Another way to express our data is that for each additional alkylated carbon beyond C$_2$, the $K_{PE,A}$ decreases by $\sim$0.8 log units. It is also possible that the faster reactivity of alkylated PAHs in the atmosphere$^{38}$ relative to their respective parent PAHs affected active and passive sampling differently.$^{39}$

**Comparison of PAH Concentrations to Other Urban Measurements.** Concentrations of $\sum_{13}$PAHs in Alexandria ranged from 390 (St 7) to 990 ng/m$^3$ (St 11) during the summer season and from 240 (St 6) to 1100 ng/m$^3$ (St 8) during the winter season. Detected PAH concentrations were higher than those measured for urban sites worldwide. In Chicago and Lake Michigan, USA, Simick et al.$^{40}$ reported vapor-phase PAH concentrations ($\sum_{26}$PAHs) of 43–200 and 4.0–50 ng/m$^3$, respectively. In Paris, Ollivon et al.$^{41}$ reported concentrations from 3.0 to 15 ng/m$^3$ ($\sum_{38}$ PAHs). In a metropolitan area in Australia, Bartkowski et al.$^{42}$ estimated a concentration of 4.0 ng/m$^3$ of $\sum_{13}$PAHs from deploying PE samplers. PAH concentrations in the present study were also higher than those detected in Toronto, Canada ($\sum_{13}$PAHs: 35–61 ng/m$^3$),$^{35}$ Belgium ($\sum_{13}$PAHs: 9.6–42 ng/m$^3$),$^{43}$ Athens, Greece ($\sum_{13}$PAHs: 6.9–120 ng/m$^3$),$^{43}$ Harbin, China ($\sum_{42}$PAHs: 6.3–340 ng/m$^3$),$^{44}$ and in Eskisehir, Turkey during the nonheating season ($\sum_{13}$PAHs: 41–290 ng/m$^3$),$^{45}$ but lower than those detected in Cairo, Egypt ($\sum_{13}$PAHs: 1900–3900 ng/m$^3$).$^6$ Detected PAH concentrations were much higher than the background level of PAHs in the ambient air of urban areas (0.15–19 ng/m$^3$).$^{46}$ Accordingly, chronic adverse health effects could possibly arise in the local residents from the exposure to PAHs in the atmospheric environment of Alexandria. Previous studies have indicated that there is a relation between the exposure to atmospheric PAHs and the possibility of development of chronic health effects (such as lung cancer).$^{46–48}$ Nevertheless, a direct comparison of PAHs between various sites should be done with caution because PAHs concentration is affected by the location of the sampling site and different sources as well as by the sampling methodology.

**Spatial Distribution and Seasonal Variations of PAHs across Alexandria.** Figure SI 9 depicts graphically the quantitative composition of the PAH mixture estimated from the PE samplers during both seasons. Similar patterns of individual PAHs were observed in all the samples during summer and winter indicating a common source of contamination with PAHs. In both seasons, samples were dominated by 2–3 rings PAHs (parent and alkylated) comprising $>$90% of the total detected concentrations. The most abundant PAHs were naphthalene (22–51%), phenanthrene (2.0–19%), and C$_{17}$-phenanthrene/anthracene (4.0–18%). Samples were more enriched with naphthalene during the winter season (39%) when compared with the summer season (29%). In the summer season, there was a marked increase in the enrichment of the samples with phenanthrene (14% compared to 9.0% in the winter samples) and C$_{17}$-phenanthrene (10%) which could be related to the increases in the evaporative emissions from petroleum products such as asphalt and coal tar sealant.$^{35}$

The spatial distribution of PAHs in Alexandria City (Figure SI 10) indicated that higher PAH concentrations were observed at sites characterized by high traffic (St 11, 2, and 3) and industrial (St 8 and 4) activities during the summer season (see Text SI 9 for more details). During the winter season, higher PAH concentrations were observed at sites characterized by industrial activities (St 8 and St 4) and heavy traffic composed mainly of heavy trucks. In all the other samples, detected PAH concentrations were relatively stable with minor variations (410–630 ng/m$^3$). This finding supports the suggestion that vehicle emissions are the major source of PAHs in the atmospheric environment of Alexandria.

No statistically significant difference was observed between detected concentrations of PAHs in the investigated samples during both seasons ($t = 0.325; p = 0.748; \alpha = 0.05$). Although combustion-derived PAH emissions may be elevated during the colder months, PAH gas-phase concentrations will be reduced by partitioning to particles which is enhanced at cold temperature. This effect will be greatest in urban areas where particle concentrations are highest. Detected concentrations of PAHs during both seasons suggest that vehicle emissions are the major sources of PAHs in Alexandria. Although unleaded petrol has recently been used, leaded gasoline is still in use, especially in old vehicles. At the same time, catalytic converters have not yet been extensively introduced to Egypt. Major contributors of vehicular pollution are four-cylinder gasoline vehicles (e.g., cars and minibuses), diesel-powered heavy vehicles (e.g., transportation buses and mini-trucks), and two-stroke-engine-powered motor cycles. The latter are powered with mixed gasoline-oil fuel to compensate for the lack of wet sump. Traffic intensities are too high for Alexandria’s inadequate road network causing congestion on busy narrow streets. Other sources of PAHs may include diesel trains, natural gas, open burning of municipal wastes, and vehicle tires.

**PAH Source Characteristics.** Concentrations and patterns of PAHs quantified in a given environment have been used to reflect their possible sources. Various molecular diagnostic ratios of PAH concentrations have been used for qualitative and quantitative characterization of sources in environmental samples.$^{42,49,50}$ However, PAH isomer ratios show substantial intrasource variability and intersource similarity$^{42}$ and should be interpreted with caution based on previous knowledge about possible sources of PAHs that exist in a given area. Molecular ratios used in this study included Ant/Ant+Phe, Phe/Ant, alkylated Phe (sum of all methylated Phen) to Phe (MPhe/ Phe), MDBT/MPhe, Phe+Ant/Phe+Ant+C$_{17}$-Phe/Ant, Flare/ Flare+Pyr, BaA/BaA+Chry, InP/InP+BghiP, and BaP/BghiP. Calculated diagnostic ratios are presented in Figure SI 11. All the calculated ratios indicated that vehicular emissions are the major source of PAHs in the atmospheric environment of Alexandria, Egypt. This is also in-line with the rather uniform concentrations across wide swaths of this major city (see Text SI 10 for more details).

**Implications.** The results of this study indicate that low-density polyethylene sheets can be successfully used to assess spatial and temporal trends of PAHs in an arid urban city. This is of great significance as it indicated how a simple, accessible, and cost-effective sampling medium can yield valuable data in developing countries because of the problems associated with conventional active air sampling techniques. Accordingly, databases regarding PAHs can be acquired to develop pollution control and management plans on the national scale. The results obtained from this study also highlighted the role of urban cities as sources of PAHs to the regional environment. This is of great importance for cities like Alexandria located on the Mediterranean coast as substantial loading to the coastal
waters could occur both through atmospheric deposition and surface runoff. Results obtained from our investigation highlighted the need for performing more studies to better understand the partitioning and equilibration mechanisms of alkylated PAHs between PEs and the surrounding atmosphere as most studies concentrated on the parent PAHs despite the higher detectable concentrations of alkylated PAHs in the atmospheric environment of urban cities worldwide.

**ASSOCIATED CONTENT**

**Supporting Information**

Details on deployments, methods, PAH concentrations, and their selected physicochemical properties, plus additional correlations. This information is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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