

Characterization and concentrations of polycyclic aromatic hydrocarbons in emissions from different heating systems in Damascus, Syria

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Received: 20 August 2013 / Accepted: 29 December 2013 / Published online: 18 January 2014
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Abstract Traffic has long been recognized as the major contributor to polycyclic aromatic hydrocarbon (PAH) emissions to the urban atmosphere. Stationary combustion sources, including residential space heating systems, are also a major contributor to PAH emissions. The aim of this study was to determine the profile and concentration of PAHs in stack flue gas emissions from different kinds of space heaters in order to increase the understanding of the scale of the PAH pollution problem caused by this source. This study set out to first assess the characteristics of PAHs and their corresponding benzo[a]pyrene equivalent emissions from a few types of domestic heaters and central heating systems to the urban atmosphere. The study, enabled for the first time, the characterization of PAHs in stationary combustion sources in the city of Damascus, Syria. Nine different types of heating systems were selected with respect to age, design, and type of fuel burned. The concentrations of 15 individual PAH compounds in the stack flue gas were determined in the extracts of the collected samples using high-performance liquid chromatography system (HPLC) equipped with ultraviolet–visible and fluorescence detectors. In general, older domestic wood stoves caused considerably higher PAH emissions than

modern domestic heaters burning diesel oil. The average concentration of Σ PAH (sum of 15 compounds) in emissions from all types of studied heating systems ranged between 43 ± 0.4 and $316 \pm 1.4 \mu\text{g}/\text{m}^3$. Values of total benzo[a]pyrene equivalent ranged between 0.61 and $15.41 \mu\text{g}/\text{m}^3$.

Keywords PAH · Benzo[a]pyrene · Heating systems · Air pollution · Toxic pollutants

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds found throughout the environment. Chemically, PAHs are a group of hydrocarbons consisting of two or more fused benzene-type rings. They are mainly produced from combustion of saturated hydrocarbon compounds (fossil fuels) under oxygen-deficient conditions. PAH and their derivatives are also associated with the incomplete combustion of organic material arising partly from natural combustion, such as volcano eruptions or forest fires, but mostly arising from anthropogenic activities, such as the burning of fossil fuels in motor vehicles, residential heating, home cooking, and industrial production activities (Li et al. 2003; Manahan 1993). PAHs are found in both vapor and particulate phases in the atmosphere. The vapor phase consists of predominantly lower molecular weight PAHs while higher molecular weight PAHs condense into very small particulate nuclei to form particulate-phase PAHs. PAHs have received increased attention in recent decades in air pollution studies because of their carcinogenicity and mutagenicity, especially benzo[a]pyrene (B[a]P) (Esen et al. 2008; Wang et al. 2009). In addition, several PAH compounds have been classified by

Responsible editor: Constantini Samara

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the International Agency for Research on Cancer as “probable” human carcinogens (2A) or “possible” human carcinogens (2B) (Poster et al. 2006). Road traffic in UK used to be a significant source of PAH emissions (Quality of Urban Air Review Group 1993). Studies had shown that up to 90 % of total PAHs (Σ PAHs) and B[a]P at roadside locations and 40 % at background locations were attributed to this source (Smith and Harrison 1996; Nielsen et al. 1996). However, updated vehicle emission inventories indicate a significant decrease in PAHs emission in England (The Department for Environment, Food and Rural Affairs 2003). This is largely due to the introduction of the Three-Way-Catalytic Converters and the production of low-emission vehicles which had significantly reduced PAHs emissions from vehicles. The carcinogenic potency associated with PAH emissions from different heating systems like domestic space heaters and central heating systems were also estimated. Domestic sources are often numerous, widespread, and small which can, under unfavorable conditions, lead to widespread population exposure sometimes at elevated levels (European Union 2001). Some studies have shown that residential coal and wood burning is a major source of inhalable particulate matter and associated mutagenic PAH in winter urban air (Freeman and Cattell 1990; Leese et al. 1989; Rogge et al. 1998; Kulkarni and Venkataraman 2000; Bari et al. 2011; Callén et al. 2013). Domestic combustion of solid fuels makes a significant contribution to the Σ PAH emissions. In Sweden, wood burning has been estimated to contribute 430 kg B[a]P in 1994, whereas gasoline and diesel vehicles together were estimated to contribute up to 320 kg B[a]P (Boström et al. 2002). Similar results have been reported for Los Angeles during winter, with a higher PAH to organic carbon ratio resulting from wood combustion than those from vehicular emissions (Ravindra et al. 2008).

The objectives of this study were to determine and compare the emissions from different combustion sources commonly used in heaters fired with diesel fuel and wood and to investigate and analyze the profiles of PAHs in the particulate and gaseous phases. This study focuses on PAH emissions from different heating system types and provides additional insights into possible health and environmental impacts of smoke pollution from the burning of fuel in different space heating systems in the city of Damascus, Syria. Considering the importance of the emission of these compounds to the atmosphere in relation to human health, the aim of this work is also to characterize and quantify the more toxic PAHs present in the stack flue gas of some residential heating systems. Till date, no data are available on the concentration and the emission profile of PAHs from residential heating systems in the city of Damascus nor in Syria and probably in the Middle East countries. Data on PAH emissions from stationary and mobile sources are very scarce and limited in the Middle East Region (Dimashki et al. 1996, 2007; Alkurdi et al. 2013).

Materials and methods

Sampling locations and types of heating systems investigated

Stack sampling experiments were conducted in Damascus is the capital of Syria located in the southwest part of the country. Damascus is reputed as “the world’s most ancient centers of civilization” and as “the oldest continuously inhabited city in the world.” Its current population is estimated between four and five million inhabitants. During winter season, the inhabitants of Damascus rely mainly on the burning of diesel oil in different types of stoves and heating systems.

PAH compounds (in both vapor phase and particle associated) were collected from the stack emissions of nine different types of space heating systems that were commonly used in Damascus, Syria. The sampling experiments were carried out during the winter season of November 2008 until February 2009. The selected space heaters were divided into three types:

Type I—central heating systems burning diesel oil: this category represents large central heating system (in New Cham residential area), large central heating system (in a governmental building, the Environmental Studies Center (ESC)), small central heating unit (in Barzeh residential area), and central heating system (small unit in a house).

Type II—traditional domestic heaters burning diesel oil: This category represented old traditional stove (type SHAMS), a household water boiler, an old space heater (type OLMAR), and a modern space heater (type OLMAR).

Type III—traditional domestic stoves burning wood.

The approximate ages of heaters ranged from 2 months to 50 years.

Table 1 shows the design and some characteristics of the residential space heaters inspected. Figure 1 shows the map of sampling locations in the city of Damascus. Table 2 lists the main properties of the diesel fuels.

At the start of each sampling experiment, the heater was set to run for a few minutes until the stack flue gas temperature and PAH concentrations had attained a steady-state condition. The stack sampling experiment from each type of heating system was repeated three times under normal operating conditions of the space heaters.

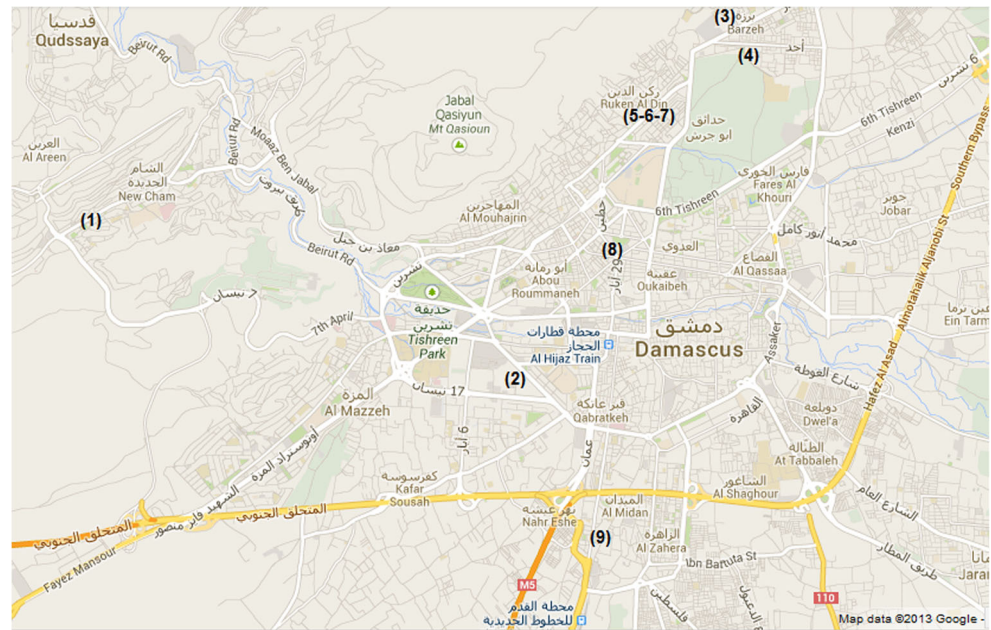
Experimental setup for PAHs source emission sampling

Before sampling, Teflon-coated glass fiber filters were cleaned with high-performance liquid chromatography system (HPLC)-grade solvents (a mixture of *n*-hexane and dichloromethane, $v/v=1:1$) in an ultrasonic bath for 180 min and baked

Table 1 Design and some characteristics of heaters

Type	Heater	Design and properties	Approximate age	Sampling duration (min)	Temperatures of flue gases (°C)	Stack height (m)	Heat output (kW)
Central heating systems	Large central heating system (in New Cham residential area)	Consists of all the pipe work and radiators that are connected to the boiler. The boiler provides the heat, but it is the pump that moves the heated water from the boiler through the pipe work to the radiators, and back to the boiler for re-heating. Fired with diesel fuel feeds almost 1,000 houses	20 years	10	82	50	30,000
	Large central heating system (in a governmental building, the Environmental Studies Center)	Consists of all the pipe work and radiators that are connected to the boiler. The boiler provides the heat, but it is the pump that moves the heated water from the boiler through the pipe work to the radiators, and back to the boiler for re-heating. Fired with diesel fuel feeds almost 120 rooms	5 years	15	67	40	835
	Small central heating unit (in Barzeh residential area)	Consists of all the pipe work and radiators that are connected to the boiler. The boiler provides the heat, but it is the pump that moves the heated water from the boiler through the pipe work to the radiators, and back to the boiler for re-heating. Fired with diesel fuel feeds almost 10 houses	25 years	10	45	21	220
	Central Heating System (small unit in a house)	Consists of all the pipe work and radiators that are connected to the boiler. The boiler provides the heat, but it is the pump that moves the heated water from the boiler through the pipe work to the radiators, and back to the boiler for re-heating. Fired with diesel fuel feeds almost 1 house	30 years	10	52	15	27–33
Traditional oil stove	Old traditional stove (type SHAMS)	Fired with diesel fuel, mead of sheet iron, shaped like cylinder, 30-cm diameter, and 75-cm height	20 years	10	78	8	4
	Household water boiler	Boiler connects to heat storage tanks (a water tank for storage of heat). Fired with diesel fuel, mead of sheet iron, shaped like cylinder, 40-cm diameter, and 50-cm height	15 years	10	43	10	7
	Old space heater (type OLMAR)	Fired with diesel fuel. Its “triple burn technology” meant that it was fitted with a ceramic plate on the top of the fire box to stop the hot air escaping to the flue before being well combusted, with a small portion of secondary air entering at the top of the fire box to ensure that total combustion of gases is achieved. This type of design supports more complete combustion, and results in reduction of smoke formation while maximizing the heat generated	10 years	16	82	8	14
Traditional wood stove	Modern space heater (type OLMAR)	Fired with diesel fuel. Its “triple burn technology” meant that it was fitted with a ceramic plate on the top of the fire box to stop the hot air escaping to the flue before being well combusted, with a small portion of secondary air entering at the top of the fire box to ensure that total combustion of gases is achieved. This type of design supports more complete combustion, and results in reduction of smoke formation while maximizing the heat generated	2 months	10	140	4	14
	Old-type domestic wood stove	Fired with poplar wood, mead of sheet iron, shaped like cylinder, 50-cm diameter, and 50-cm height	50 years	10	35	13	6

Fig. 1 Map of sampling locations in the city of Damascus. 1, Large central heating system (in New Cham residential area). 2, Large central heating system (in a governmental building, the ESC). 3, Small central heating unit (in Barzeh residential area). 4, Central Heating System (small unit in a house). 5, Old Traditional Stove (type SHAMS). 6, Household Water Boiler. 7, Old space heater (type OLMAR). 8, Modern space heater (type OLMAR). 9, Old-type domestic wood stove



in a muffle furnace at about 200 °C to eliminate trace organic contaminants. The conditioned filters were then wrapped in aluminum foil (that had been rinsed with hexane) and sealed in a clean glass jar capped with Teflon-lined caps. Polyurethane foam (PUF) cartridges were also cleaned with *n*-hexane for 24 h in a Soxhlet apparatus to ensure they were free from contamination. Following extraction, PUF plugs were drained out and placed in the oven at 60 °C for 2 h to evaporate the residual solvent. After drying, PUF plugs were individually wrapped in hexane-washed aluminum foils, placed in clean screw-capped jars with Teflon cap liners, and

stored in the refrigerator at 4 °C until sampling (Smith and Harrison 1996; Dimashki et al. 1996; Dimashki 1998; Alkurdi et al. 2013).

Flue gas samples from heaters stack were collected from the stack using a PAH sampling train composed of a sampling probe with a stainless steel filter holder, followed by a stainless steel cylinder to accommodate three PUF plugs a flow meter and a vacuum pump. Stack emission sampling lasted from about 10 to 16 min and the temperatures of flue gases varied from 35 to 140 °C. As PAHs in the stack gases are semivolatile, measurements for both particle phase and gas

Table 2 The main physicochemical properties of the diesel fuel

Specification	Requirement	Analytical method
Diesel		
Density (g/ml at 15 °C)	0.860–0.820	ASTM D-1298/90
Flash point (°C min)	60	ASTM D-93
Viscosity (cSt at 37.8 °C)	2.5–4.5	ASTM D-445/88
Sulfur content (wt.%)	0.7	ASTM D-1266/87
Aniline point (°C)	65	ASTM D-611/82(1987)
Diesel index	53–56	IP 21/81
Pour point (°C max)	(–10) °C	S.N.S 176/2000
Ash content (wt.% max)	0.01	ASTM D-482/87
Water and sediment (vol.% max)	0.05	ASTM D-2709/88
Acids and alkalis	NIL	ASTMD-664/89
Carbon residue (Conrad son; wt.% max)	0.1	ASTMD-189/88
CFPP (cold filter plugging point; °C max)	(–2) summer and (–5) winter	IP 309
Distillation:		
Volume recovered at 360 °C (vol.% min)	85	ASTMD-86/90
50 % recovers at 290 °C max		

phase were necessary. The most widely used method for trapping gas-phase PAHs is adsorption on plugs of polyurethane foam (PUF) placed behind the filter (Keller and Bidleman 1984; Chuang et al. 1987; De Raat et al. 1987; Benner et al. 1989; Hawthorne et al. 1992; Dimashki 1998). This method is widely accepted because of the low pressure drop, low blanks, low cost, and ease of handling. Teflon-coated glass fiber filter (TX40HI20WW Pallflex, Putnam, Connecticut, USA, retention efficiency <99.0 % for particles 0.035–1 μm) held in stainless steel filter holder and placed in ahead of the three PUF plugs (10 cm each), were used to ensure the complete collection of particle-associated and vapor-phase PAH, respectively (Ristovski et al. 2005; Lim et al. 2005; Dimashki 1998). In order to avoid water condensation in the sampling system, the device was placed as close as possible to the stack. The sampling point was positioned at the end of the stack (De Abrantes et al. 2004) and heater stack samples were collected after ensuring thermal equilibrium between the stack flue gas and the probe. A vacuum pump (MILLIPORE, 75 mmHg) was installed behind the flow meter (1–5 l/min) to draw the stack gas sample from the stack. During sampling, the stack gas was sampled through the sampling train at a sampling flow rate of approximately 3 l/min (Alkurdi et al. 2013). The sampling setup is shown in Fig. 2.

Given their volatility, some breakthrough of the lower molecular weight and more volatile PAH compounds has been observed when using PUF plugs (Billings and Bidleman 1980; You and Bidleman 1984). In this study, breakthrough tests were conducted using three stages of PUF cartridges placed in series, each of which was individually analyzed and compared in terms of the PAH mass collected. The results showed that the average ΣPAH mass distribution was as follows: 75.2 % was collected on the first PUF plug, 20.3 % on the second PUF plug and 4.5 % on the third PUF plug, suggesting that PAH breakthrough would be negligible after the 3rd PFU plug.

In order to obtain statistically significant emission data and minimize random experimental errors, three replicate sampling runs were conducted during each stack gas sampling experiment. The mean concentration of individual PAHs in stack emission was then calculated from the analysis of the three replicate samples collected from the stack flue gas stream

Sample extraction and analysis

Sample extraction and analysis were performed according to USEPA method TO-13 (USEPA 1999). After sample collection, the PTFE-coated filters and polyurethane foam plugs were wrapped in aluminum foil to avoid sample degradation from ultraviolet (UV) light and stored at -17 °C until the extraction. The samples were never stored for more than 10 days (de Abrantes et al. 2004). Each emission sample, including the filter and the three PUF plugs, were extracted together in the same Soxhlet extractor (500 ml capacity) with 300 ml dichloromethane (HPLC grade; purity, >99.8 %) for about 24 h (5–6 cycles/h). During extraction, the Soxhlet apparatus was wrapped in aluminum foil to protect the sample against light. The volume of the sample extract was reduced to about 5 ml using a rotary evaporator at 36 °C, and finally, the volume was brought down to about 1 ml under a gentle stream of high-purity nitrogen. Following extraction, the extracts were cleaned in order to eliminate interferences from polar compounds and sampling artifacts. Sample cleanup was performed on a solid-phase extraction cartridge and entailed removal of water, solid debris, and interfering compounds by passing the sample extract through a column packed with silica SepPak mesh no. 60, topped with 1 cm of anhydrous sodium sulfate. The eluate was transferred to 1.5 ml vials and evaporated to near complete dryness under a gentle flow of high purity nitrogen and re-dissolved with 1 ml of high purity HPLC-grade acetonitrile before analysis.

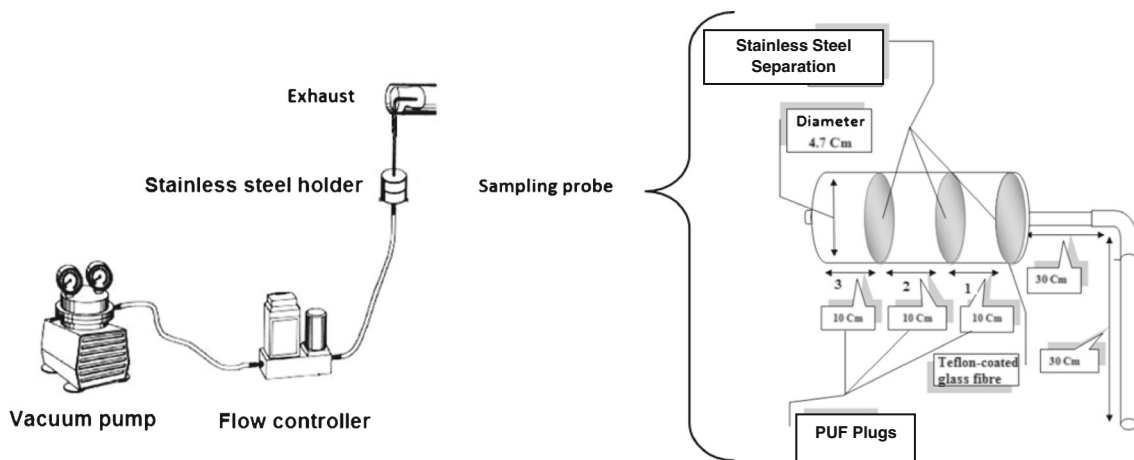


Fig. 2 Sampling setup

Fifteen PAH compounds (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, B[a]P, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene) were identified and quantified using HPLC system (Agilent 1100 HPLC) equipped with fluorescence and UV detectors connected in series. The identification and quantification of individual PAH compounds in the cleaned samples extracts were performed using the external standard method (Smith and Harrison 1996; Dimashki et al. 1996; Dimashki 1998). The HPLC system was calibrated before and after the analysis of each batch of samples using a standard solution containing known concentrations of individual PAH compounds. The use of the internal standard method for the identification and quantifications of PAHs would have been far better, however, this was not possible for several reasons including the unavailability of deuterated PAH standards in Syria and the inherent problems of HPLC analytical method for its poor peak separation and the co-elution of parent PAH compounds with deuterated PAH standards in comparison with the high resolution power of capillary columns in GC/MS analysis.

Quality assurance/quality control

Quality assurance/quality control was conducted in order to minimize and quantify sampling and analytical measurement errors by carrying out field and laboratory blanks, standard-spiked recoveries, HPLC calibration curves, and detection limits. PAHs standard mixture solution (2,000 ppm at more than 99 % purity in acetonitrile) for the 16 PAH compounds specified in USEPA Method 610 was obtained from AccuStandard USA (DIN 38414-23 PAH). Working standard solutions in the concentrations range from 1 to 10 ng/μl of each PAH were prepared by the dilution of the standard stock solution, and the standard calibration curves were prepared over the entire concentration range. Daily working standards of PAH standard mixture solution were freshly prepared at frequent intervals and stored in the dark at 4 °C. These standards were then used to calibrate the HPLC instrument. Recovery efficiencies for individual PAH compounds were determined by spiking blank samples (filter and PUF plugs) with measured amounts of a standard solution containing known PAH concentrations and following the same experimental procedures used for sample extraction, cleanup, and HPLC analysis. Recovery runs were processed with each batch of samples to ensure the integrity and daily variations in the analytical works. A standard reference material obtained from NIST (SRM-1597) was also used to check the recovery efficiency of individual PAH compounds. Results of the recovery tests showed that the recovery efficiency the 15 PAH compounds varied between 60 and 89 %. The percent recovery must fall between 60 and 120 % to be acceptable (USEPA

1999). In general, lower recoveries were associated with the lower molecular-weight PAH, especially naphthalene. Data reported in the study were all corrected for recoveries. Field and laboratory blank samples (for both filters and PUF cartridges) were also processed with each batch of samples. Analysis of blank samples showed no significant contamination with PAH compounds (HPLC UV-visible and fluorescence integrated area < detection limit). The lower limit of detection for each PAH compound was calculated from the signal-to-noise ratio of the individual peak assuming a minimum detectable signal of 2 (S/N=2). The minimum detection limit (MDL) for individual PAH compounds ranged from 0.5 ng/100 μl for benzo[k]fluoranthene to 2.9 ng/100 μl for acenaphthene.

Optimizing the HPLC analysis

Fifteen individual PAH compounds were identified and quantified by means of reverse-phase HPLC using UV-visible and fluorescence detectors in series. The extracted samples were filtered prior to HPLC analysis using Gelman Nylon Acrodisc 0.2 μm syringe filters. Good chromatographic separation of the 15 PAH compounds was achieved by employing a PAH-specific reverse-phase HPLC column (Hypersil Green PAH with corresponding guard column, Shandon Scientific, Runcorn, Cheshire, UK). Several parameters were tested in order to decide upon the optimal conditions for the HPLC analysis of the 15 PAH compounds. Table 3 lists the optimum excitation and emission wavelengths for individual PAHs. The details of instrumental specifications and chromatographic conditions used for the HPLC analysis are shown in Table 4.

Table 3 Programmed wavelength fluorescence detection of PAHs

Elution order	PAH compound	Excitation wavelength (nm)	Emission wavelength (nm)
1	Naphthalene	270	333
2	Acenaphthene	245	350
3	Fluorene	245	350
4	Phenanthrene	297	340
5	Anthracene	295	430
6	Fluoranthene	260	430
7	Pyrene	260	430
8	Benz[a]anthracene	260	430
9	Chrysene	260	430
10	Benzo[b]fluoranthene	297	430
11	Benzo[k]fluoranthene	297	430
12	Benzo[a]pyrene	297	430
13	Dibenz[a,h]anthracene	297	430
14	Benzo[g,h,i]perylene	297	430
15	Indeno[1,2,3-cd]pyrene	297	430

Table 4 Instrumental specification and chromatographic conditions employed during the PAH analysis by HPLC with UV–vis and fluorescence detection

HPLC system	
Agilent 1100 HPLC System Liquid Chromatograph	
100 μl sample injection loop	
Hypersil Green 5 μm PAH column (4.6 mm i.d. \times 15 cm)	
Hypersil Green PAH guard column	
Agilent 1100 UV–visible detector (at 290)	
Chromatographic conditions	
Mobile phase (acetonitrile and distilled deionized water)	
Oven temperature (35 $^{\circ}\text{C}$)	
Equilibration time (10 min)	
Pump flow rate (1,200 $\mu\text{l min}^{-1}$)	
Detectors outputs (Chemstation)	
Gradient elution program	
Step 1=constant 50 % (acetonitrile) for 5 min	
Step 2=linear gradient from 50 to 100 % (acetonitrile) over 35 min	
Step 3=constant 100 % (acetonitrile) for 5 min	
Step 4=100 to 50 % (acetonitrile) for 10 min	

HPLC analysis of cleaned sample extracts was performed in triplicates.

Results and discussion

Results of individual PAH compounds

All 15 PAH compounds studied were identified and quantified in the sample extracts of stacks emissions. Table 5 presents the average concentration of individual PAH compounds measured in the flue gas emission of different domestic heating systems in the city of Damascus, Syria. For the first type central heating systems five PAH compounds (naphthalene, fluorene, fluoranthene, pyrene, and B[a]P) had the highest concentrations in the tests performed. On average, the sum of naphthalene, fluorene, and fluoranthene emission rates amounted to 67.79 % of ΣPAH emissions. For this type of domestic heater, naphthalene participation averaged 37.71 % and fluorene 15.45 % in relation to the sum of ΣPAH compounds. Similarly, fluoranthene and pyrene averaged 14.62 and 7.51 %, respectively. Whereas the second type of traditional oil domestic heater had the highest five PAH compound concentrations (naphthalene, fluorene, fluoranthene, pyrene, and anthracene) in the tests performed. On average, the sum of naphthalene, fluorene, and fluoranthene emission rates amounted to 78.12 % of ΣPAH emissions. For this type, naphthalene participation averaged 45.91 % and fluorene 21.18 % in relation to the sum of ΣPAH compounds. Similarly, fluoranthene and pyrene averaged 11.03 and

5.15 %, respectively. For the third type of traditional wood domestic stove, five PAH compounds (naphthalene, phenanthrene, fluoranthene, benzo[b]fluoranthene, and benz[a]anthracene) had the highest concentrations in the tests performed. On average, the sum of naphthalene, phenanthrene and fluoranthene emission rates amounted to 78.85 % of ΣPAH emissions. For this type naphthalene participation averaged 30.48 % and phenanthrene 30.42 % in relation to the sum of ΣPAH compounds. Similarly, fluoranthene and benzo[b]fluoranthene averaged 17.94 % and 3.9 %, respectively. The other PAH compounds exhibited irregular behavior. Regularity in the percentile emission of the most frequent PAH in relation to the sum of PAH is evident. The MDL, the minimum concentration of a substance that can be measured and reported with confidence and that the value is above zero, for the individual 15 PAH compounds, including naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, B[a]P, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene was found to be 24.73, 0.87, 5.06, 0.19, 0.35, 0.13, 0.59, 0.15, 0.06, 0.48, 0.16, 0.27, 0.1, 0.22, and 0.34 $\mu\text{g}/\text{m}^3$, respectively.

Results of total PAHs emission

ΣPAHs concentration (sum of 15 PAH compounds), mean concentration, and standard deviation of the total emission (both gas and particle phases) for individual PAH compounds in the stack flue gas of different heating systems in the city of Damascus are presented in Table 5 for the purpose of comparing the various PAHs emission loads to the atmosphere from different domestic heating systems.

The magnitudes of ΣPAH concentrations for the nine different types of heating systems were ranged from 43 ± 0.4 to 316 ± 1.4 $\mu\text{g}/\text{m}^3$ in the following order: modern space heater type OLMAR (43 ± 0.4 $\mu\text{g}/\text{m}^3$) < central heating system small unit in a house (57 ± 0.3 $\mu\text{g}/\text{m}^3$) < old space heater type OLMAR (67 ± 0.4 $\mu\text{g}/\text{m}^3$) < small central heating unit in Barzeh residential area (101 ± 0.4 $\mu\text{g}/\text{m}^3$) < old traditional stove type SHAMS (102 ± 0.2 $\mu\text{g}/\text{m}^3$) < large central heating system in a governmental building, the ESC (107 ± 0.3 $\mu\text{g}/\text{m}^3$) < household water boiler (114 ± 1.1 $\mu\text{g}/\text{m}^3$) < large central heating system in New Cham residential area (166 ± 0.5 $\mu\text{g}/\text{m}^3$) < old-type domestic wood stove (316 ± 1.4 $\mu\text{g}/\text{m}^3$).

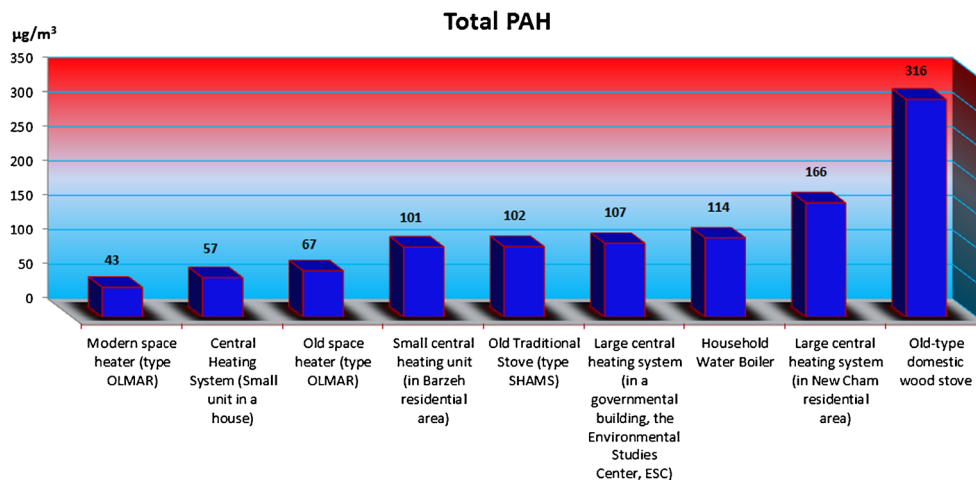
Data obtained in this study showed that the highest ΣPAHs concentration was associated with stack emissions from old-type domestic stoves burning poplar wood. This value is considerably higher than the average concentrations generated by other heating system (i.e., household water boiler) which fired with diesel fuel and the average concentrations which were obtained for other heating system (i.e., old traditional stove (type SHAMS)) which fired with diesel fuel. At the

Table 5 Mean concentration (gas and particulates) of individual PAH compounds in flue gas emission of different domestic heating systems in the city of Damascus, Syria (micrograms per cubic meter, $n=3$)

PAH compound	Modern space heater (type OLMAR)		Central heating system (small unit in a house)		Old space heater (type OLMAR)		Small central heating unit (in Barzeh residential area)		Old traditional stove (type SHAMS)		Large central heating system (in a governmental building, the Environmental Studies Center)		Household water boiler		Large central heating system (in New Cham residential area)		Old-type domestic wood stove	
	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C (g/m^3)	SD (%)	C (g/m^3)	SD (%)	C (g/m^3)	SD (%)	C (g/m^3)	SD (%)	C (g/m^3)	SD (%)
Naphthalene	27.65	0.9	26.10	1.2	45.14	1.3	68.53	1.5	25.79	0.9	42.96	1.12	51.20	4.3	24.73	1.3	96.27	1.1
Acenaphthene	0.87	0.09	2.25	0.05	4.55	0.5	6.267	0.05	2.34	0.01	3.48	0.05	2.24	0.03	3.16	0.07	1.95	0.03
Fluorene	10.59	1.1	5.06	0.09	12.71	1	6.78	0.05	35.57	0.5	39.67	0.9	10.21	0.2	15.00	1.2	5.24	0.08
Phenanthrene	0.29	0.04	1.98	0.09	1.21	0.09	0.19	0.01	3.43	0.03	4.64	0.06	4.9	0.09	3.73	0.03	96.09	4
Anthracene	0.35	0.02	2.86	0.07	0.6	0.03	5.44	0.04	3	0.03	1.91	0.09	8.22	0.1	4.93	0.08	5.67	0.06
Fluoranthene	0.13	0.01	4.74	0.1	0.16	0.01	1.53	0.06	15.08	0.1	0.91	0.08	20.61	0.4	55.75	0.5	56.68	4.1
Pyrene	0.84	0.02	3.28	0.09	0.59	0.02	1.45	0.09	4.32	0.05	1.14	0.09	11.05	0.2	26.44	0.7	7.46	0.3
Benzo[a]anthracene	0.26	0.02	0.82	0.03	0.15	0.01	0.86	0.02	0.95	0.04	0.30	0.01	0.91	0.02	1.36	0.09	10.21	0.9
Chrysene	0.31	0.03	0.42	0.03	0.06	0.01	0.44	0.03	0.59	0.02	0.13	0.01	0.77	0.03	1.25	0.04	3.65	0.02
Benzo[b]fluoranthene	0.48	0.02	2.91	0.07	0.58	0.03	3.04	0.09	3.01	0.09	1.03	0.03	0.95	0.07	3.40	0.08	12.33	1.3
Benzo[k]fluoranthene	0.19	0.01	0.67	0.02	0.16	0.01	0.78	0.03	0.68	0.03	4.32	0.08	0.90	0.09	8.88	0.9	2.01	0.04
Benzo[a]pyrene	0.27	0.02	2.68	0.08	0.47	0.04	2.74	0.01	2.69	0.08	5.04	0.07	1.06	0.07	13.06	1	7.83	0.05
Dibenz[a,h]anthracene	0.16	0.01	0.50	0.02	0.1	0.01	0.57	0.04	0.52	0.01	0.18	0.01	0.15	0.01	0.58	0.03	0.56	0.01
Benzo[g,h,i]perylene	0.30	0.01	1.25	0.08	0.22	0.02	1.3	0.09	1.25	0.05	0.42	0.03	0.58	0.01	1.39	0.07	4.75	0.04
Indeno[1,2,3-cd]pyrene	0.34	0.02	1.56	0.09	0.37	0.02	1.19	0.08	2.48	0.09	0.43	0.04	0.67	0.02	2.01	0.09	5.16	0.07
Total PAHs	43	0.4	57	0.3	67	0.4	101	0.4	102	0.2	107	0.3	114	1.1	166	0.5	316	1.4

SD standard deviation

Fig. 3 Comparison of ΣPAH concentrations (sum of 15 compounds) in stack emissions from various heating systems in Damascus, Syria



same time, PAH content in emissions from the old space heater (type OLMAR) is rather low compared with the old-type wood stove, oxygen deficiency, and low temperature also could be the reason of the incomplete combustion wood in old fireplaces. On the other hand the results of PAH concentration from the central heating systems also show their small emissions in comparison with wood combustion. It can also be noted that emission from large-scale central heating systems in NEW SHAM is considerably higher than the average concentrations of E.S.C, central heating system in buildings, prefabricated BARZEH and the average concentrations of central heating system small unit in one house.

Figure 3 compares the concentration of ΣPAH (sum of 15 PAH compounds) in stack emission of different heating systems in Damascus, Syria.

Toxicity assessment and B[a]P_{eq} contained in the stack emissions of space heaters

Table 5 shows that naphthalene contributed to the majority of ΣPAH for all types of heaters. Therefore, the measurements of ΣPAH might be deceptive in assessing the health risks associated with the exposure to ΣPAH because some PAH compounds such as: B[a]P, DBA, B[a]A, B[b]F, B[k]F and IND are more carcinogenic than naphthalene. Therefore, we examined the emission of B[a]P equivalent (BaP_{eq}) as a health risk estimate from the exposure to PAH. Investigation of PAH emissions will be incomplete without assessing the carcinogenic potency of individual PAH compounds in heaters stack emissions. The International Agency for Research on Cancer (2003) has classified B[a]P, B[a]A, and DBA as probable human carcinogens (2A) and B[b]F, IND, naphthalene and B[k]F as possible human carcinogens (2B). All other PAH compounds are currently regarded as ‘not classifiable’ (Poster et al. 2006). As B[a]P has been known to be the most carcinogenic PAH compound, the carcinogenic potency of each collected sample was also determined relative to its BaP_{eq}

concentration (B[a]P_{eq}). The B[a]P_{eq} for a given PAH compound was calculated as the product of its toxic equivalent factor (TEF) and its concentration (Chen et al. 2006).

Because toxicity criteria are not available for all PAHs, various TEFs have been proposed in order to relate the potencies of these compounds to that of B[a]P, which is regarded as one of the most carcinogenic PAHs (Lim et al. 2007). There

Table 6 TEFs developed by different agencies

PAH compound	MOE (1997)	USEPA (1993)	CEPA (1994)	Cal EPA (1993)	Nisbet and LaGroy (1992)
Naphthalene	— ^a	— ^a	— ^a	— ^a	0.001
Acenaphthylene	— ^a	— ^a	— ^a	— ^a	0.001
Acenaphthene	— ^a	— ^a	— ^a	— ^a	0.001
Fluorene	— ^a	— ^a	— ^a	0.01	0.001
Phenanthrene	0.00064	— ^a	— ^a	— ^a	0.001
Anthracene	0.28	— ^a	— ^a	0.1	0.01
Fluoranthene	— ^a	— ^a	— ^a	0.01	0.001
Pyrene	0.0	— ^a	— ^a	0.1	0.001
Cyclopenta[<i>c,d</i>]pyrene	— ^a	— ^a	— ^a	— ^a	— ^a
Benzo[<i>a</i>]anthracene	0.014	0.145	— ^a	0.1	0.1
Chrysene	0.026	0.0044	— ^a	0.01	0.01
Benzo[<i>b</i>]fluoranthene	0.11	0.167	0.06	0.1	0.1
Benzo[<i>k</i>]fluoranthene	0.037	0.020	0.04	0.1	0.1
Benzo[<i>e</i>]pyrene	— ^a	— ^a	— ^a	— ^a	— ^a
Benzo[<i>a</i>]pyrene	1.0	1	— ^a	— ^a	1
Perylene	— ^a	— ^a	— ^a	— ^a	— ^a
Indeno[1,2,3- <i>cd</i>]pyrene	0.067	0.055	0.12	0.1	0.1
Dibenzo[<i>a,h</i>]anthracene	0.89	1.11	— ^a	— ^a	1
Benzo[<i>b</i>]chrysene	— ^a	— ^a	— ^a	— ^a	— ^a
Benzo[<i>ghi</i>]perylene	0.012	— ^a	— ^a	0.01	0.01
Coronene	— ^a	— ^a	— ^a	— ^a	— ^a

^a No TEF has been suggested

Table 7 Average concentrations of benzo[a]pyrene equivalent (micrograms per cubic meter)

PAHs compound	Modern space heater (type OLMAR)		Central heating system (small unit in a house)		Old space heater (type OLMAR)		Small central heating unit (in Barzeh residential area)		Old traditional stove (type SHAMS)		Large central heating system (in a governmental building, the Environmental Studies Center)		Household water boiler		Large central heating system (in New Cham residential area)		Old-type domestic wood stove	
	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)	C ($\mu\text{g}/\text{m}^3$)	SD (%)
Naphthalene	0.02765	9.10^{-4}	0.0261	12.10^{-4}	0.04514	13.10^{-4}	0.06853	15.10^{-4}	0.02579	9.10^{-4}	0.04296	112.10^{-5}	0.0512	43.10^{-4}	0.02473	13.10^{-4}	0.09627	11.10^{-4}
Acenaphthene	0.00087	9.10^{-5}	0.00225	5.10^{-5}	0.00455	5.10^{-4}	0.006267	5.10^{-5}	0.00234	1.10^{-5}	0.00348	5.10^{-5}	0.00224	3.10^{-5}	0.00316	7.10^{-5}	0.00195	3.10^{-5}
Fluorene	0.01059	11.10^{-4}	0.00506	9.10^{-5}	0.01271	1.10^{-3}	0.00678	5.10^{-5}	0.03557	5.10^{-4}	0.03967	9.10^{-4}	0.01021	2.10^{-4}	0.015	12.10^{-4}	0.00524	8.10^{-5}
Phenanthrene	0.00029	4.10^{-5}	0.00198	9.10^{-5}	0.00121	9.10^{-5}	0.00019	1.10^{-4}	0.00343	3.10^{-5}	0.00464	6.10^{-5}	0.0049	9.10^{-5}	0.00373	3.10^{-5}	0.09609	4.10^{-3}
Anthracene	0.0035	2.10^{-4}	0.0286	7.10^{-4}	0.006	3.10^{-4}	0.0544	4.10^{-4}	0.03	3.10^{-4}	0.0191	9.10^{-4}	0.0822	1.10^{-3}	0.0493	8.10^{-4}	0.0567	6.10^{-4}
Fluoranthene	0.00013	1.10^{-5}	0.00474	1.10^{-4}	0.00016	1.10^{-5}	0.00153	6.10^{-5}	0.01508	1.10^{-4}	0.00091	8.10^{-5}	0.02061	4.10^{-4}	0.05575	5.10^{-4}	0.05668	4.10^{-4}
Pyrene	0.00084	2.10^{-5}	0.00328	9.10^{-5}	0.00059	2.10^{-5}	0.00145	9.10^{-5}	0.00432	5.10^{-5}	0.00114	9.10^{-5}	0.01105	2.10^{-4}	0.02644	7.10^{-4}	0.00746	3.10^{-4}
Benzo(a)anthracene	0.026	2.10^{-3}	0.082	3.10^{-3}	0.015	1.10^{-3}	0.086	2.10^{-3}	0.095	4.10^{-3}	0.030	1.10^{-3}	0.091	2.10^{-3}	0.136	9.10^{-3}	1.021	9.10^{-2}
Chrysene	0.0031	3.10^{-4}	0.0042	3.10^{-4}	0.0006	1.10^{-4}	0.0044	3.10^{-4}	0.0059	2.10^{-4}	0.0013	1.10^{-4}	0.0077	3.10^{-4}	0.0125	4.10^{-4}	0.0365	2.10^{-4}
Benzo(b)fluoranthene	0.048	2.10^{-3}	0.291	7.10^{-3}	0.058	3.10^{-3}	0.304	9.10^{-3}	0.301	9.10^{-3}	0.103	3.10^{-3}	0.095	7.10^{-3}	0.340	8.10^{-3}	1.233	13.10^{-2}
Benzo(k)fluoranthene	0.019	1.10^{-3}	0.067	2.10^{-3}	0.016	1.10^{-3}	0.078	3.10^{-3}	0.068	3.10^{-3}	0.432	8.10^{-3}	0.090	9.10^{-3}	0.888	9.10^{-2}	0.201	4.10^{-3}
Benzo(a)pyrene	0.27	2.10^{-2}	2.68	8.10^{-2}	0.47	4.10^{-2}	2.74	1.10^{-2}	2.69	8.10^{-2}	5.04	7.10^{-2}	1.06	7.10^{-2}	13.06	1	7.83	5.10^{-2}
Dibenz(a,h)anthracene	0.16	1.10^{-2}	0.50	2.10^{-2}	0.1	1.10^{-2}	0.57	4.10^{-2}	0.52	1.10^{-2}	0.18	1.10^{-2}	0.15	1.10^{-2}	0.58	3.10^{-2}	0.56	1.10^{-2}
Benzo(g,h,i)perylene	0.0030	1.10^{-4}	0.0125	8.10^{-4}	0.0022	2.10^{-4}	0.013	9.10^{-4}	0.0125	5.10^{-4}	0.0042	3.10^{-4}	0.0058	1.10^{-4}	0.0139	7.10^{-4}	0.0475	4.10^{-4}
Indeno[1,2,3-cd]pyrene	0.034	2.10^{-3}	0.156	9.10^{-3}	0.037	2.10^{-3}	0.119	8.10^{-3}	0.248	9.10^{-3}	0.043	4.10^{-3}	0.067	2.10^{-3}	0.201	9.10^{-3}	0.516	7.10^{-3}
Total	0.61	3.10^{-3}	3.86	8.10^{-3}	0.77	4.10^{-3}	4.05	5.10^{-3}	4.06	8.10^{-3}	5.95	7.10^{-3}	1.75	7.10^{-3}	15.41	8.10^{-2}	11.77	2.10^{-2}

SD standard deviation

are also different TEFs developed by different agencies and scientists, some of them are listed in Table 6.

The TEFs developed by Nisbet and LaGoy (1992) were proved to be a better set of TEF values (Petry et al. 1996) and were most commonly used by scientists while assessing the carcinogenic potency of PAH mixtures (Tsai et al. 2001), see, e.g., (Petry et al. 1996; Mi et al. 2001). The TEFs estimated by Nisbet and LaGoy (1992) were adopted in this study, the toxicity potencies (B[a]P_{eq}) of each PAH were determined by multiplying the emission factors of the PAH with its toxicity equivalent factor (BaP_{eq}=TEF×PAH concentration) (Nisbet and LaGoy 1992). The total B[a]P_{eq} for emission from each heater was obtained by summing B[a]P_{eq} for each PAH compound found in the flue gas. Table 7 shows the average concentrations of B[a]P_{eq} for each of the individual 15 PAH compounds and the total B[a]P_{eq} for each type of heater.

Figure 4 presents the profile of total B[a]P_{eq} concentrations (micrograms per cubic meter) in heaters stack.

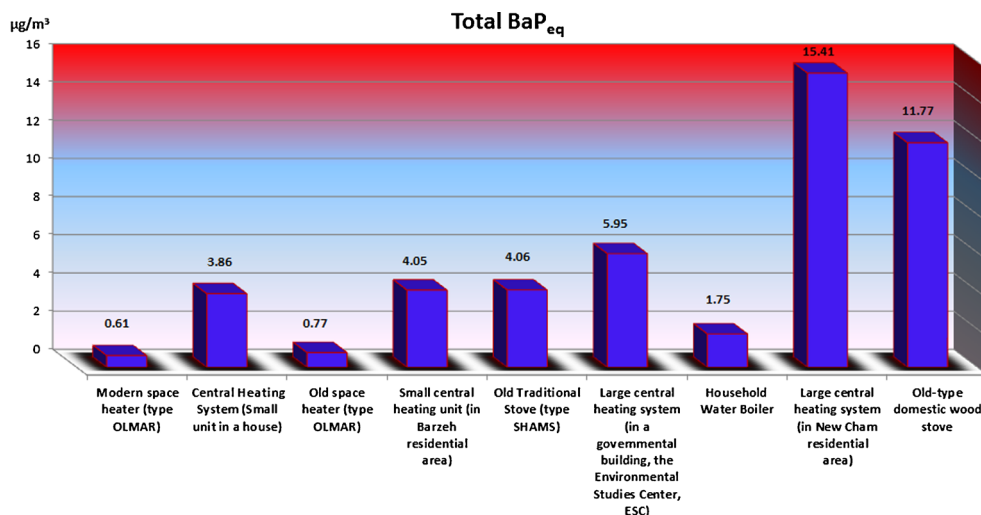
These results show the importance of three factors in reducing ΣPAH emissions, and thus the total equivalents B[a]P_{eq} emitted from heater. The first is the kind of fuel, the second is the design of heater especially those central heating systems that feeds more than one house, and the third is the age. It is evident from the results obtained in this study that Traditional Wood Domestic stove (Old-type domestic wood stove) produced much higher average ΣPAH emission (316 μg/m³) and total BaP_{eq} (11.77 μg/m³) when compared with the much less average ΣPAH emission (43 μg/m³) and total BaP_{eq} (0.61 μg/m³) produced by Traditional Oil domestic heater (Modern OLMAR Domestic heater). In addition, Traditional Oil domestic heater (Old OLMAR Domestic heater) produced 67 μg/m³ and 0.77 μg/m³ of average ΣPAH emission and total BaP_{eq}, respectively. However, for central heating systems, the average ΣPAH emission and the total B[a]P_{eq} emitted from large-scale central heating systems in NEW SHAM were 166 and 15.41 μg/m³ respectively, that

feeds almost 1000 houses, that mean for one house it will be 0.17 and 0.02 μg/m³, for central heating system at the ESC were 107 and 5.95 μg/m³ respectively, that feeds almost 120 rooms, that mean for one room it will be 0.89 and 0.05 μg/m³ and the same thing from small-scale central heating system, prefabricated buildings BARZEH were 101 and 4.05 μg/m³ respectively, that feeds almost 10 houses, that mean for one house it will be 10.1 and 0.41 μg/m³, which are much less compared with emissions from central heating system (small unit in one house) were 57 and 3.86 μg/m³, respectively.

Very large differences in emissions were observed between traditional domestic heater and modern central heating systems. In particular, high emissions of the B[a]P_{eq} were recorded for Old-type domestic wood stove and Traditional Oil domestic heater, which are the ones most frequently installed in houses today.

The lower emissions of PAH compounds from diesel fuel heaters in comparison with wood stoves were expected. Emissions of the B[a]P_{eq} from traditional wood domestic stove could be reduced by using traditional diesel oil domestic heater (i.e., old traditional stove (type SHAMS)) up to about 3 times and up to about 15 times for old space heater (type OLMAR) and up to about 19 times for modern space heater (type OLMAR) and up to 7 times for Household Water Boiler. Consequently, a traditional wood domestic stove may have at least more than three times as high an impact on health as other types. Also emissions of the B[a]P_{eq} could be reduced by using central heating systems (i.e., large-scale central heating systems in NEW SHAM) up to about 764 times and up to about 237 times for central heating system at the ESC and up to about 29 times for small-scale central heating system, prefabricated buildings BARZEH and up to about 3 times for central heating system small unit in one house. However, the use of wood in our country for heating is still reduced when most houses shift to using heaters fired

Fig. 4 Comparison of ΣBaP_{eq} (micrograms per cubic meter) concentrations (sum of 15 compounds) in stack emissions from various heating systems in Damascus, Syria



with diesel fuel, but sometimes when the price of fuel rises some homes goes back to using wood for heating.

Valuable information on PAHs emissions and their characteristics from fuel burning have been obtained from this study. These results can be used as inputs and suggestions for appropriate policy and guidelines of fuel combustion-related heating.

Conclusions

This study enabled, for the first time, the characterization of 15 PAH compounds emitted from nine different heating systems in the city of Damascus, Syria. Stationary sources tested in this study include the following: a traditional domestic heater burning wood, four traditional domestic heaters burning diesel oil, and three central heating systems burning diesel oil. Σ PAH emission values ranged from 43 to 316 $\mu\text{g}/\text{m}^3$, and total BaP_{eq} values ranged from 0.61 to 15.41 $\mu\text{g}/\text{m}^3$. PAH emissions from heating systems were dramatically reduced when using central heating systems supplied with fuel dosing and excess air for combustion. PAH concentration varies significantly depending on the type of fuel and domestic heater design. The highest levels of PAH emission were measured from old-type domestic stoves burning wood. PAHs content in emissions from the Traditional Oil domestic heater is higher than in emissions from the central heating systems. The lowest levels of PAH emission are from large-scale central heating systems in New Cham residential area. As an example, substitution of the old-type domestic wood stove with a modern central heating system could reduce BaP_{eq} up to about 764 times. Most domestic space heaters installed in Damascus and other cities in Syria are of the old traditional stove (type SHAMS) which does not have any control of air to fuel ratio, causing high soot formation and higher emissions of PAH compounds (102 $\mu\text{g}/\text{m}^3$) in comparison with modern domestic space heaters “OLMAR” equipped with fuel dosing system and excess air for combustion (43 $\mu\text{g}/\text{m}^3$). It is recommended from both environmental and health point of view that these old traditional stove type domestic heaters are to be replaced with modern residential heating systems.

Stack sampling experiments conducted in this study were performed without measuring the amount of burnt fuel, therefore, it was not possible to calculate the PAHs emission factors per unit volume or mass of fuel burned. It is recommended in future studies to calculate the emission factors for individual PAH compounds and the Σ PAHs emission factor per unit of fuel burned

Acknowledgments The authors would like to thank Mrs. Rawnak Jabour for her valuable contribution in the analytical works throughout the study. Thanks are also due to Mr. Brian Freeman for his valuable

technical advice. This work was included in a thesis submitted for a M.Sc. degree by the first author. Funding for this research was provided by the ESC and Damascus University.

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