



## Charcoal emissions as a source of CO and carcinogenic PAH in mainstream narghile waterpipe smoke

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### ABSTRACT

Burning charcoal is normally placed atop the tobacco to smoke the narghile waterpipe. We investigated the importance of charcoal as a toxicant source in the mainstream smoke, with particular attention to two well-known charcoal emissions: carbon monoxide (CO) and polycyclic aromatic hydrocarbons (PAH). CO and PAH yields were compared when a waterpipe was machine smoked using charcoal and using an electrical heating element. The electrical heating element was designed to produce spatial and temporal temperature distributions similar to those measured using charcoal. With a popular type of *ma'assel* tobacco mixture, and using a smoking regimen consisting of 105 puffs of 530 ml volume spaced 17 s apart, it was found that approximately 90% of the CO and 75–92% of the 4- and 5-membered ring PAH compounds originated in the charcoal. Greater than 95% of the benzo(a)pyrene in the smoke was attributable to the charcoal. It was also found that the relative proportions of individual PAH species, the “PAH fingerprint”, of the mainstream smoke were highly correlated to those extracted from the unburned charcoal ( $R^2 > 0.94$ ). In contrast, there was no correlation between the PAH fingerprint of the electrically heated and charcoal-heated conditions ( $R^2 < 0.02$ ). In addition to inhaling toxicants transferred from the tobacco, such as nicotine, “tar”, and nitrosamines, waterpipe smokers thus also inhale large quantities of combustion-generated toxicants. This explains why, despite the generally low temperatures attained in the narghile tobacco, large quantities of CO and PAH have been found in the smoke.

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### 1. Introduction

The narghile waterpipe (Fig. 1) has enjoyed a popular revival in recent years, attracting new smokers within and outside of its traditional geographic and demographic domains. Some researchers (Rastam et al., 2004) attribute the recent rise in its popularity to the marketing and availability of *ma'assel*, a heavily sweetened and flavored tobacco mixture that lists “molasses” as an ingredient. When *ma'assel* is smoked, it releases an aroma of caramelizing sugar. Probably due to its high moisture content, the tobacco does not burn in the self-sustaining manner that characterizes the cigarette. To sustain the smoke generation process, a continuous heat source – normally burning charcoal – is placed on top of the tobacco at the start of a use session, and is replaced or adjusted one or more times to subjectively maintain the “strength” of the smoke while avoiding over-charring the tobacco. In fact, we have previously found in a clinical study of 29 *ad libitum* waterpipe smokers (Shihadeh et al., 2006) that, by mass, generally more charcoal is consumed during a narghile use session than is tobacco. As a result, smokers and those in their company inhale charcoal combustion

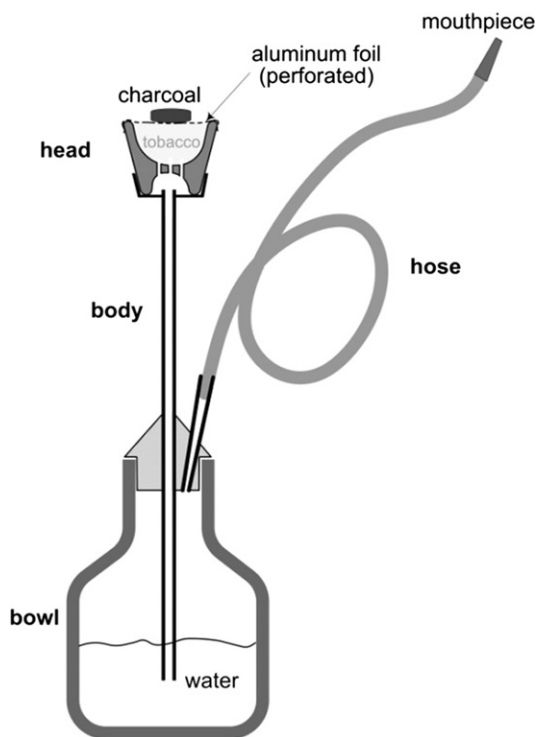
emissions in addition to the constituents released from the tobacco mixture.

We have previously measured alarmingly high levels of carcinogenic PAH (Sepetdjian et al., 2008) and CO (Shihadeh and Saleh, 2005) in mainstream narghile smoke despite the fact that the maximum temperatures reached in the narghile tobacco are likely too low to support the reactions required to form these compounds (Shihadeh, 2003). Given that burning charcoal has been previously found to emit CO and PAH (e.g. Dyremark and Westerholm, 1995), it is reasonable to speculate that charcoal is the major source of these compounds in narghile smoke. If so, this would indicate the need for studies of narghile toxicant yield to account for variations in charcoal usage by smokers – not only for its effect on the tobacco, but as a source of toxins itself.

This study thus focuses on the role of charcoal as a unique toxicant source in narghile smoking. In particular, the relative contributions of the charcoal and tobacco to CO and PAH yields in mainstream narghile smoke are assessed by comparing yields when the narghile is smoked with charcoal to those when it is smoked using an equivalent electrical heating source. The differences in yields between these two conditions can be considered the contribution of the charcoal. CO and PAH were selected because they respectively represent components of the smoke that

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**Fig. 1.** Schematic of a narghile waterpipe in the *ma'assel* configuration. The head (fired clay), body (metal or wood), water bowl (metal or glass), and corrugated hose (leather or nylon stretched over a wound flexible wire coil support) are the primary elements from which a narghile is assembled. Tobacco is loaded into the head, where several large holes in the base allow the smoke to pass into the central conduit of the body that leads to the water bowl. When a smoker inhales through the hose, a vacuum is created in the space above the waterline, causing smoke to bubble into the water bowl from the body. When *ma'assel* – a mixture of tobacco, sweeteners, and other flavorings – is smoked, the head is filled with 10–20 g of the tobacco mixture and covered with an aluminum foil sheet that is perforated for air passage. Burning charcoal is placed on top of the aluminum foil.

are considered major causative agents in cardiovascular disease and lung cancer (Hoffmann et al., 1997).

## 2. Methods

The approach taken in this study was to compare PAH and CO yields in the mainstream smoke of the narghile when it was smoked with and without the charcoal. For the no charcoal condition, an electrical heater was designed which provided temporal and spatial temperature distributions in the tobacco similar to the case where charcoal was used. Thus the objectives of this study included characterizing heat transfer phenomena in the narghile head, developing an electrical analog to the charcoal, and measuring CO and PAH yield for the two conditions. A third condition in which charcoal would be used without tobacco in the narghile head was considered for data triangulation, however preliminary experiments showed that none of the PAH analytes originating in the charcoal were detectable at the narghile mouthpiece. Subsequent mathematical modeling of the aerosol transport mechanics in the narghile showed that nanometer sized incipient PAH particles require the near micron-sized tobacco smoke particles for efficient transport to the mouthpiece; the model showed that PAHs rapidly coagulate with and then “ride” the tobacco smoke condensates from the head to the mouthpiece. Without the tobacco smoke condensates “carrying” them, the PAH particles, due to their small size and resulting high diffusivity, are effectively stripped from the flow by diffusional deposition on the interior surfaces of the narghile. Thus the charcoal-only condition was eliminated because the atypical particle transport mechanics would invalidate the results.

### 2.1. Temperature measurements

Temperature was recorded at three locations in the head (Fig. 2): at the coal–tobacco interface ( $T_1$ ), at a depth of 1 cm in the tobacco ( $T_2$ ), and at the head outlet ( $T_3$ ). These were chosen to indicate, respectively, the peak temperatures reached in the tobacco, the degree of heat penetration from the hot coal, and the bulk thermal energy carried by the gas exiting the head. Rapid-response Type J thermocou-

ples (0.25 mm diameter) were automatically sampled at a rate of 10 Hz using a PC-based National Instruments PCI 6040E data acquisition card. Thermocouples were located along the head's axis of symmetry, and were threaded through stainless steel tubes cemented in the clay head.

### 2.2. Smoking protocol

A digitally controlled waterpipe smoking machine (described in Shihadeh and Azar, 2006) was used to smoke the narghile using a steady periodic puffing regimen consisting of 105 puffs of 2.6 s duration, 17 s interpuff interval, and 0.53 l puff volume. Except for the number of puffs, these parameters were chosen based on a model derived from smoking topography measurements of 52 smokers in a Beirut café (Shihadeh et al., 2004). The number of puffs used was reduced from the model's 171 to 105 to correspond to the approximate puff number at which a single charcoal briquette is consumed (Shihadeh and Saleh, 2005). Ten grams of *ma'assel* tobacco mixture (Two Apples flavor, Nakhla brand, Egypt) was loaded in the head, and covered with a single  $9 \times 9$  cm aluminum sheet perforated using the 18 hole pattern specified in Shihadeh (2003). When charcoal was used, a single easy-lighting charcoal briquette (Three Kings Charcoal Co., Holland) weighing 5.8 g was lit, held for 60 s in a vertical position, and then placed on the loaded waterpipe head.

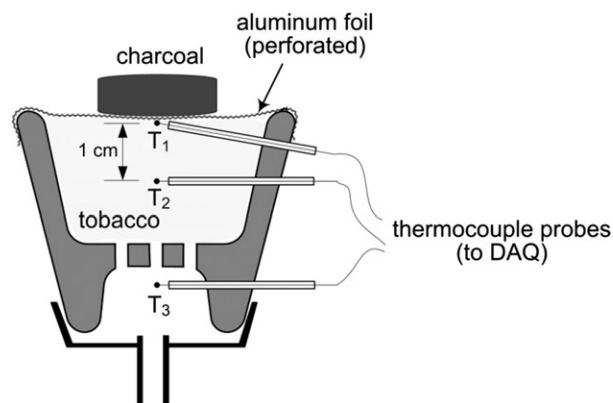
It should be noted that these easy-light charcoal briquettes are commonly used in narghile smoking and, at least in Lebanon, are invariably sold wherever narghile tobacco is sold. Smokers rely on them when convenience dictates, since lighting only requires a match or lighter be held to it for a few seconds. Nonetheless, we estimate that while self-lighting charcoal disks are used in an important fraction of narghile smoking sessions, the majority of narghile smoking in Lebanon, especially in restaurants and cafés, is done using a traditional charcoal which is inherently heterogeneous in size and shape. In the interest of generating reproducible data and simplifying the procedures, we used the standard quick-lighting charcoal disks.

### 2.3. Smoke collection and analysis

The smoke aerosol was sampled using the setup described in Shihadeh and Saleh (2005). Briefly, the smoke issuing from the narghile mouthpiece was split into two parallel streams, and each passed through a 47 mm glass fiber filter (Gelman Type A/E) to trap the particle phase. The filters were changed at 40, 60, and 80 puffs to avoid overloading, resulting in four pairs of filter samples for each smoking session. Downstream of the filters circa 1% of the flow was sampled by a diaphragm pump that was automatically actuated during each puff. The pump exhausted into an inert grab sampling bag, whose contents were analyzed using an electrochemical CO meter (Bacharach, Monoxor II) at the end of each smoking session. Because the CO is a gas-phase component, the particle filters located upstream of the sampling location do not affect the CO concentration.

Total particulate matter (TPM) yield was determined by pre- and post-weighing each filter assembly (filter + holder). Tobacco consumed during each smoking session was also determined gravimetrically by weighing the narghile head (without the heating source) before and after smoking.

For PAH determination, each filter was sonicated in 15 ml of toluene, and the resulting solution was concentrated under a flow of nitrogen. The concentrated solution was eluted with 10 ml of hexane through a conditioned SPE cartridge, and evaporated to 1 ml under a flow of nitrogen. The resulting solutions for each group of 4 filters (constituting all the filters of a single flow branch from a given smoking session) were combined as a single sample and evaporated to dryness under a flow of nitrogen. The solid phase was reconstituted in 0.1 ml of acetonitrile and analyzed by GC–MS. Chromatographic separation was achieved with an Alltech ATTM-5ms column (30 m  $\times$  0.25 mm, 0.25  $\mu$ m film thickness), using helium gas as the carrier phase. Quantification was done in the selected ion current mode. Additional details of the procedure are described in Sepetdjian et al. (2008).



**Fig. 2.** Schematic of the experimental waterpipe head. Thermocouples junctions are centered along the head axis of symmetry.

#### 2.4. Electric heater development

The electric heater was developed iteratively using various heater elements, materials, geometries, thermal contact resistances, and power input schedules. For all the considered designs, heat was delivered through a metal disk of circular cross-section with diameter equal to that of the charcoal briquette (Fig. 3). Criteria used in designing the electrical heater included mimicking the tobacco temperatures in the head and matching the TPM yielded per gram of tobacco consumed ("TPM yield ratio") to those measured with the base charcoal heating condition.

We found it crucial to consider the modes by which charcoal transfers heat to the tobacco to arrive at the desired TPM yield ratio. Normally, thermal energy from the charcoal is transported by conduction between puffs, and by additional convection of hot combustion gases during a puff. (Order of magnitude calculations show that radiative transfer to the tobacco is negligible here.) While initial electrical heater designs produced the desired temperatures at  $T_1$ , heat transport to  $T_2$  and  $T_3$  was found to be inadequate. When the power input was increased to boost  $T_2$  and  $T_3$ , tobacco consumption increased, but TPM actually decreased. We found that the tobacco was over-charred near  $T_1$ , and that particulate matter could be visually observed escaping through the top of the perforated aluminum foil between puffs; the electric heater was boiling off the volatiles through the top of the head rather than into the drawn smoke, resulting in lower mainstream TPM yields. Normally, no smoke visibly emanates from the narghile head between puffs.

Attention was therefore turned to reducing the rate of heat conduction from the electrical heater – and therefore the heat delivered between puffs – and increasing the heat delivered by convection of hot air during a puff. To do so, the weight of the heater assembly was reduced to increase contact resistance and passages were incorporated into the metal disk to improve air flow through the heater during a puff. The final design incorporated a steel wire mesh between the heater assembly and the aluminum foil cover of the head. The mesh allowed air to easily flow between the heater and waterpipe head, while also serving to reduce conductive heat transfer from heater to head. With this increased resistance to conductive transfer, the problem of "cooking" the tobacco between puffs was eliminated, and the temperature of the heater could be increased sufficiently to ensure that the air passing under it became hot enough to deliver a significant pulse of convective thermal energy each puff. This resulted in good thermal penetration into the head, and temperature profiles and TPM yield ratios that similar to those when charcoal was used.

The final heater design utilized a  $2.7 \Omega$  heating element mounted on a brass disk, as shown in Fig. 3. Electric power from a DC power supply was delivered to the coil through the body of the heater assembly. A constant voltage was applied during each smoking session.

Preliminary experiments indicated that the great majority of the CO and PAH originated from the charcoal rather than the tobacco. Therefore before proceeding with further measurements of CO and PAH, we increased the electrical power input to the heater such that the lower bound of the tobacco temperature envelope generated with the electric heater approximately corresponded to the upper bound of that of the base charcoal condition. By doing so, the maximum potential toxicant emissions from the tobacco would be measured. Because the charcoal contribution is calculated by subtracting the toxicant yields of the electrically heated condition from those of the base condition, a conservative estimate would thus be obtained for the role of the charcoal as a toxicant source. The temperature envelopes, calculated as the instantaneous mean  $\pm$  SEM temperature for eight repeated trials of each heating condition, are shown in Fig. 4.

#### 2.5. Data analysis

Arithmetic mean and standard error of the mean were calculated for each repeated measurement. To identify the sources of PAH in the smoke, mean yields of the target PAH compounds for the two experimental conditions were compared to one another and to previously published data. The comparisons were made by

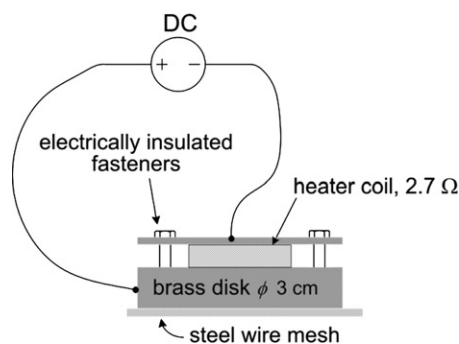


Fig. 3. Schematic of the electrical heater apparatus used in this study.

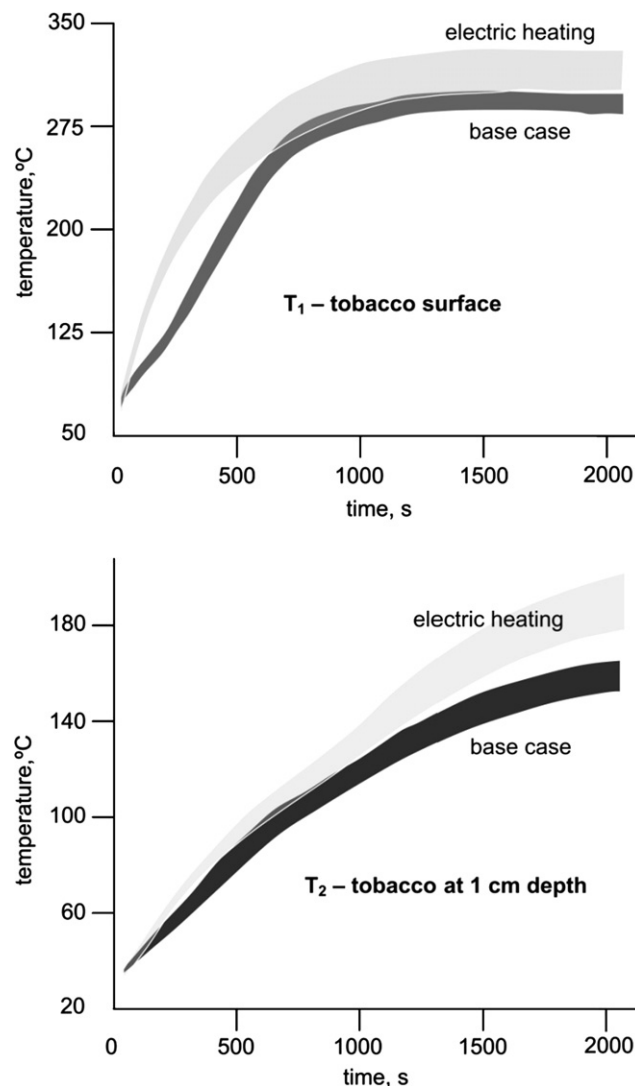


Fig. 4. Measured temperature envelopes for electrical and charcoal heating conditions at (a) tobacco surface and (b) 1 cm below surface. Temperature envelopes correspond to the mean  $\pm$  SEM calculated at every 100 ms interval for eight repeated trials in each condition.

calculating the square of the Pearson product-moment correlation coefficient ( $R^2$ ) resulting from comparing the mean yields of the target PAH compounds from one experimental condition and previously published data to another.

### 3. Results

#### 3.1. TPM and tobacco burned

The tobacco consumed and TPM yield ratio are given for the electric heating and charcoal heating cases in Table 1. It can be seen that the electrically heated condition had greater tobacco consumption and TPM yield, consistent with its elevated tobacco

Table 1

Tobacco consumed, TPM yield, and yield ratio (mean  $\pm$  SEM) for base case and electrical heating condition

N = 8	Base case	Electrical heating
Tobacco consumed, mg	3004.2 $\pm$ 535.2	3842.8 $\pm$ 610.7
TPM yield, mg	774.7 $\pm$ 210.8	880.5 $\pm$ 223.8
Yield ratio, mg TPM/mg tobacco	0.21 $\pm$ 0.03	0.22 $\pm$ 0.03

temperature (Fig. 4), though the TPM yield ratio was the same as for the base condition, indicating similar heat and mass transport processes.

**Table 2**  
Normalized PAH yields for the two smoking conditions and for raw charcoal extracts

	Narghile smoke (N = 5)		Charcoal extract (N = 2), ng/g charcoal <sup>a</sup>
	Base case, ng/mg TPM	Electrical heating, ng/mg TPM	
Acenaphthalene	0.121(0.031)	0.032(0.005)	1.49(0.05)
Acenaphthylene	0.281(0.122)	0.257(0.052)	7.43(0.01)
Fluorene	0.260(0.029)	0.143(0.024)	20.16(0.74)
Phenanthrene	1.649(0.365)	0.260(0.059)	86.89(13.22)
Anthracene	0.298(0.044)	0.166(0.033)	13.48(0.33)
Fluoranthene	1.339(0.303)	0.320(0.065)	71.50(5.90)
Pyrene	1.313(0.483)	0.265(0.031)	95.14(3.22)
Chrysene + Benzo(a)anthracene	0.368(0.086)	0.098(0.040)	33.40(1.09)
Benzo(k+b)fluoranthene	0.209(0.063)	<0.038	4.41(0.13)
Benzo(a)pyrene	0.219(0.042)	<0.010	9.62(1.81)
Benzo(g,h,i)perylene	0.138(0.053)	<0.056	2.58(0.32)
Dibenz(a,h)anthracene	0.115(0.027)	<0.024	1.73(0.32)
Indeno(123-cd)pyrene	0.133(0.063)	<0.064	2.37(0.15)

Values reported as mean ± SEM.

<sup>a</sup> Quantities reported for charcoal do not include extraction efficiency/recovery and thus represent a lower bound estimate.

**Table 3**  
Summary of findings

	Base	Electrically heated	Charcoal contribution (%)
CO, mg	57.2	5.7	90
PAHs, ng/mg TPM			
Benzo(a)pyrene	0.219	<0.01	>95
Σ 2- and 3-ring PAH	5.262	1.444	73
Σ 4- and 5-ring PAH	1.181	0.098–0.290 <sup>a</sup>	75–92

Charcoal contribution determined by difference between base and electrically heated conditions.

<sup>a</sup> This range includes the summation of the limits of quantification for those compounds whose concentrations were too low to be quantified.

### 3.2. Carbon monoxide

CO yields for the base and electrically heated conditions were  $57.2 \pm 4.79$  and  $5.70 \pm 2.07$  mg, respectively. CO yield thus dropped by circa 90% when the charcoal was removed.

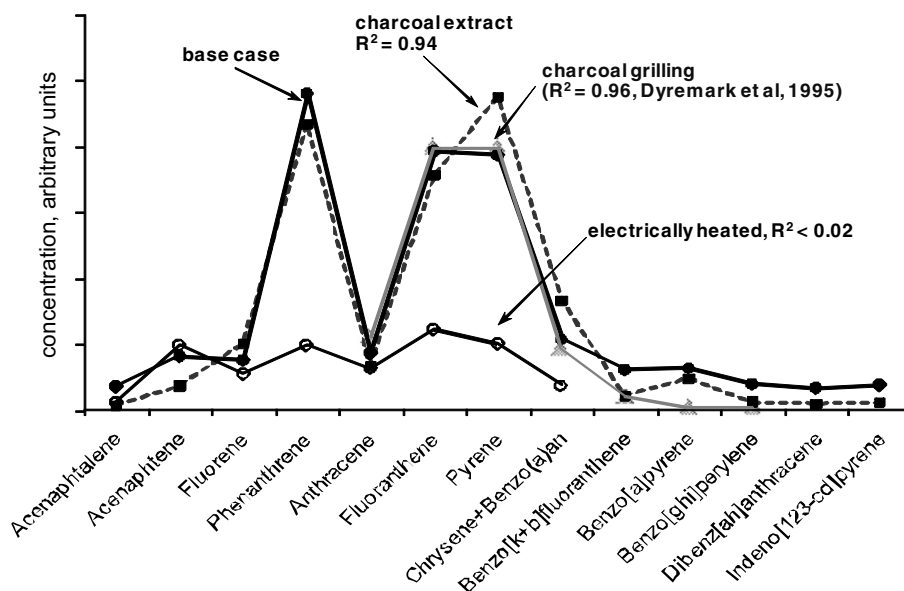
### 3.3. PAHs

The PAH yields in the mainstream smoke for the two experimental conditions are given in Table 2 and summarized in Table 3. The base condition provided significantly greater PAH yields than the electric heater condition. Without charcoal, yields for all of the carcinogenic 4- and 5-ring compounds dropped to below detectable limits.

Also reported in Table 2 are PAHs found in samples of unburned charcoal extracts. Thus in addition to *in situ* pyrosynthesis, PAHs may be introduced to the mainstream aerosol by desorption of pre-existing PAHs (i.e. residuals from the charcoal manufacturing process) as the narghile is smoked. It should be noted that the quantities of PAHs reported for the charcoal in Table 2 assume extraction efficiencies of 100%; in all likelihood, the extraction efficiency is considerably less, meaning that the values reported for charcoal represent lower bounds. It should also be noted that similar levels of PAHs were measured for two samples of traditional hardwood charcoal (*sindyan*) commonly used to smoke narghile in Lebanon.

## 4. Discussion

This study was undertaken to address the role of charcoal in producing narghile mainstream smoke toxicants. For this purpose, CO and PAHs, both thought to originate in the pyrolysis and combustion reactions likely most prevalent in the charcoal, were selected for analysis. Other toxicants such as nicotine and tobacco specific nitrosamines clearly originate in the tobacco, and were not studied here. Limitations of this study include restricting the experimental matrix to a single type of charcoal, tobacco, and smoking regimen to generate the smoke.



**Fig. 5.** Relative PAH concentrations measured in the mainstream smoke of the base and electrically heated conditions, and in extracts of the unburned charcoal. PAH concentrations from smoke collected from a charcoal grill by Dyremark and Westerholm (1995) shown for comparison. Correlation coefficients are shown relative to the base condition. Unburned charcoal extract, charcoal grilling smoke, and base case narghile smoke exhibit similar PAH patterns. Electrically heated condition produces a different PAH pattern.

The results are summarized in Table 3, where it can be seen that charcoal is responsible for the majority of the PAH and CO content of the smoke. This finding is consistent with the slow pyrolysis kinetics expected at the relatively low temperatures prevalent in the tobacco (Ledesma et al., 2002).

The distribution of PAH concentrations in the mainstream smoke and unburned charcoal extracts are shown graphically in Fig. 5, where it can be seen that the PAH composition for the base condition closely resembles that of the unburned charcoal extract. An  $R^2$  of 0.94 is obtained when the compound-by-compound charcoal PAH concentrations are correlated to those for the base smoking condition. These PAH distributions also bear remarkable similarity to PAH emissions measured from a charcoal-burning food grill (Dyremark and Westerholm, 1995), also shown in Fig. 5. Correlation of the PAH data reported by Dyremark and Westerholm (1995) to that of the base case in the current study yields an  $R^2$  of 0.96. In contrast, the PAH distribution for the electrically heated condition is uncorrelated ( $R^2 < 0.02$ ) to that of the base condition. Simply put, narghile smoke PAH profiles closely resemble those emitted from burning charcoal, not tobacco.

The high correlation between the PAH distributions of narghile smoke condensates, unburned charcoal extracts, and charcoal grill emissions provide strong corroborating evidence of the charcoal origin of the PAHs measured in narghile smoke. These compounds may be synthesized as the charcoal burns on the narghile head, or transferred to the smoke by desorption of PAH residues left on the char surface from the charcoal manufacturing process.

## 5. Conclusions

This study has demonstrated that the high yields of CO and PAHs in mainstream narghile smoke mainly derive from the charcoal. Thus, not only is the production of tobacco-derived particulate matter sensitive to variations in charcoal application (as shown by Shihadeh and Saleh, 2005), but the charcoal is itself an important toxicant source for narghile users and those in their company. Though this study focuses on toxicants generated by the charcoal, we do not suggest that the charcoal poses the only important risks to smokers; toxicants transferred from the tobacco,

such as nicotine, “tar”, and carcinogenic nitrosamines may present equally or more important health hazards.

## Conflict of interest statement

The authors declare that there are no conflicts of interest.

## Acknowledgements

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