Carcinogenic PAH in waterpipe charcoal products

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Abstract

Because narghile waterpipe (shisha, hooka) smoking normally involves the use of burning charcoal, smoke inhaled by the user contains constituents originating from the charcoal in addition to those from the tobacco. We have previously found that charcoal accounts for most of the polyaromatic hydrocarbons (PAH) and carbon monoxide in the smoke of the waterpipe, both of which are present in alarming quantities. Because charcoal manufacturing conditions favor formation of PAH, it is reasonable to assume that charcoal sold off the shelf may be contaminated by PAH residues. These residues may constitute a significant fraction of the PAH inhaled by the waterpipe user and those in her/his vicinity. We measured PAH residues on three kinds of raw waterpipe charcoal sampled from Beirut stores and cafés. We found that PAH residues in raw charcoal can account for more than half of the total PAH emitted in the mainstream and sidestream smoke, and about one sixth of the carcinogenic 5- and 6-ring PAH compounds. Total PAH content of the three charcoal types varied systematically by a factor of six from the charcoal with the least to the greatest PAH residue. These findings indicate the possibility of regulating charcoal carcinogen content.

Keywords

narghile; shisha; hooka; carcinogen; product regulation

1. INTRODUCTION

Smoking tobacco using a *narghile* waterpipe (aka shisha, hooka; see Figure 1 of Daher et al., 2010) has become a popular phenomenon world-wide, particularly among youth (e.g. Pärna et al., 2008;Baska et al., 2008;Eissenberg et al., 2008;El-Roueiheb et al., 2008;Jawaid et al., 2008;Weglicki et al., 2008;Primack et al., 2009). Users appear to be lured by the highly aromatic and sweetened tobacco paste known as *ma'ssel*, which typically contains approximately 25 wt% tobacco and a similar amount of glycerol (Rees et al., 2007). As a pre-packaged product sold using modern marketing methods, *ma'ssel* is relatively recent

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development and its introduction in this form in the 1990s may have contributed to the rocketing popularity of waterpipe smoking since then (Maziak et. al., 2004), involving many new and young smokers.

Because of its high moisture content, *ma'ssel* does not burn in a self-sustaining fashion as does cigarette tobacco; it requires a continuous external heat source to produce the smoke. Normally, the heat source used is burning charcoal, which is placed atop the *ma'ssel*. Thus the smoke inhaled by the waterpipe user includes charcoal combustion products in addition to constituents emanating from the *ma'ssel*. Mainstream and sidestream waterpipe smoke has been found to contain alarmingly high quantities of carcinogenic PAH, CO, volatile aldehydes, ultrafine particles and other toxicants (Sepetdjian et al., 2008; Al Rashidi et al., 2008; Shihadeh & Saleh, 2005; Daher et al., 2010). By comparing smoke composition produced using electrical and charcoal heating methods we have also found (Monzer et. al., 2008) that charcoal contributes most of the CO and PAH found in waterpipe smoke, both of which are delivered in quantities far exceeding those delivered by a single cigarette.

Because charcoal production involves wood pyrolysis under conditions which are favorable for PAH formation (e.g. Barbosa et. al., 2006), there is good reason to suspect that the charcoal sold to waterpipe users is contaminated by PAH. When used with a waterpipe, some of these residues are likely to be transferred to the inhaled smoke. Indeed, we previously found (Monzer et. al., 2008) that the distribution pattern of PAH compounds in waterpipe smoke closely correlated with the pattern found in unburned charcoal extracts, suggesting that a source of PAH in waterpipe smoke may be desorption of PAH residues, in addition to any PAH which may be pyrosynthesized during smoking.

The current study was conducted to examine the PAH content of three charcoal products commonly used in Lebanon for waterpipe smoking, and to explore the implications of recent developments in thought about tobacco regulation as it could apply to waterpipe products. The WHO Study Group on Tobacco Regulation (TobReg) has in recent years (see Burns et. al., 2008) advocated an approach to regulating tobacco products based on the precautionary principle:

> Wherever possible, this approach moves towards a general reduction of known harmful constituents of any product to the extent technically feasible, as part of good manufacturing processes. It does not require that, for the substance under consideration, there be proof of a specific linkage between a lower level (amount) of any individual constituent and a lower level of human disease (response). It merely requires that the substance be known to be harmful and that processes exist for its diminution or removal. (WHO, 2007)

This approach empowers regulators to require measurement of toxicant emissions from products found on the market, and to stipulate upper limits of a given toxicant when a) systematic variation exists across products, and b) manufacturing processes can be modified to limit the toxicant. If these conditions are met, TobReg recommends that regulators index upper limits to the values found for the products with the least toxicant content or emissions. Thus one impetus for this study is to probe whether PAH content systematically varies across waterpipe charcoal products. This information can also inform nascent efforts currently underway in the International Standards Organization to develop a standard narghile waterpipe testing protocol.

Charcoal used in waterpipe smoking is generally sold as formed briquettes or as lump charcoal. The briquettes are formed by compressing pulverized charcoal in a press with a binder (e.g. starch), or by pyrolyzing extruded logs formed from biomass particles (e.g. ground coconut shells). Some briquette products are "easy-light" and contain an ignition

agent. Lump charcoal, in contrast, comes in a variety of irregular shapes traceable in form to the original biomass used to make it (e.g. tree branches). The latter are commonly made by small producers using traditional kilns. In this study we examined PAH content of traditional lump charcoal, as well as two charcoal briquette products (Three Kings™, Holland; CocoNara™, Lebanon) commonly sold in Lebanon. The Three Kings™ brand contains an ignition agent, while the CocoNara™ and lump charcoal products do not. According to its packaging, CocoNara™ is manufactured from coconut shell, and is "environmentally friendly" and "100% natural".

Because PAH content may depend on the type of raw material used (Stumpe-Viksna et al., 2008), and to conditions of pyrolysis such as the heating rate, peak temperature, moisture content, and pyrolysis pressure (Antal and Grønli, 2003), there is reason to expect that PAH content can systematically vary across charcoal products.

2. METHODS

2.1. Chemicals and materials

Sixteen EPA priority PAH standard mixture of 2 mg/ml in methylene chloride and five deuterated-PAH internal standards (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, perylene-d12) were obtained from Absolute Standards (USA). The silica solid phase extraction (SPE) cartridges (1000 mg/8 ml capacity) used for sample cleaning were obtained from Alltech (USA). Solvents of analytical grade were purchased from Sigma–Aldrich.

2.2. Charcoal sample collection and preparation

The ISO/FDIS 8243 (ISO, 2006) method for cigarette sampling was adapted to collect CocoNara™ and Three Kings™ charcoal samples. Among other purposes, this ISO method is intended to provide a representative sample of a given cigarette product in a given market at a particular time. In accordance with the method, four packages of each charcoal product were collected from ten retail outlets in municipal Beirut (i.e. 40 packages of each brand were procured in total). Following ISO 4387:199(E), one package of each type was chosen randomly, and five pieces of charcoal were taken from it. The five pieces were ground and well-mixed and 5 g was taken to form a single sample. This procedure was repeated three times to make three different random samples each of CocoNara™ and Three Kings™ charcoal from the same 40 store-bought packages.

Lump charcoal used for waterpipe smoking was purchased from ten waterpipe-serving cafés in municipal Beirut. Samples were prepared by randomly selecting equal quantities of charcoal from five of the ten cafés, grinding, mixing, and selecting a 5 g sample for analysis. This procedure was repeated three times to form three different random samples of lump charcoal from the ten café batch. All samples were collected in February 2009.

2.3. PAH extraction and cleaning

Internal deuterated standards were added to 5g of each charcoal type and extracted with 15 ml of toluene for two hours at 30°C by sonication. The obtained solutions were filtered and preconcentrated using a flow of nitrogen. The volume was reduced to approximately 1 ml. An SPE silica cartridge was used to clean the sample and PAHs were collected using 10 ml of hexane. The sample was then concentrated by reducing the volume down to 150 µl using a flow of nitrogen. The sample was then injected on GC-MS.

2.4. Detection and quantification

A Thermo Trace GC-Ultra equipped with ITQ-900 ion trap MS and AI-3000 auto-injector was used in this study. Chromatographic separation was done using Thermo TR-5 ms column (30 m, 0.25 mm ID, 0.25 µm film thickness). The helium flow was 1 ml/min and 1µl of the sample was injected in a splitless mode. The injector temperature was set at 280°C and the oven temperature program was set at an initial temperature of 80°C for 4 min, then heated to 170°C at 10°C/min, increased to 180°c at 3°C/min, to 270°C at 10°C/min, and finally to 300°C at a rate of 3°C/min where it was held for 3 min. The transfer line temperature between the GC and MS was maintained at 280°C. The mass spectrometric detection was performed using an electron impact ionization mode with an ionizing energy of 70 eV and scanning from m/z 100 to 300 in a full scan mode, with an ion source temperature of 225°C. Sample chromatograms are shown in Figure 1, where it can be seen that individual compound peaks were well-resolved except for benzo(b)- and benzo(k)-fluoranthene. These chromatogram peaks were therefore combined and reported as benzo(b +k)fluoranthene. Calibration curves for the 16 PAHs were generated using PAHs standard of (0.1-0.2-0.5-1-1.6 ppm) ratios to the deuterated (0.5 ppm) PAHs in the selected ion current profile (SICP) as a function of the PAH concentration (per CORESTA Recommended Method 58, 2004). The R^2 ranged between 0.991 and 0.999.

2.5 Statistical analysis

Mean and 95% confidence intervals were computed using two-tailed Student's t-distribution. Uncertainties in total PAH were calculated using a first-order error propagation method (Figliola and Beasley, 1995).

3. RESULTS AND DISCUSSION

Results for the 16 EPA priority PAH quantified in the three charcoal products are given in Table 1. It can be seen that all the charcoal products tested contained significant quantities of PAH residues, including benzo(a)pyrene, an International Agency for Research for Cancer (IARC) Group 1 carcinogen, and that the quantities varied widely across charcoal types. The total PAH mass per gram of CocoNara™ briquette was more than 6 times that of the lump charcoal. The large intra-product variability in naphthalene however resulted in overlap in 95% confidence intervals of total PAH mass between the Three Kings™ and both of the other charcoal types. Removing naphthalene from the total, the differences in PAH mass between all three charcoal products attained statistical significance at the 95% confidence level (bottom of Table 1). Differences in the sums of 5- and 6-membered ring PAH compounds (i.e. those appearing below chrysene in Table 1), are less drastic, with the CocoNara™ containing about two times the quantities of the lump charcoal. As shown, differences between Three Kings™ and the lump charcoal were not statistically significant for the sum of 5-and 6-ring PAH compounds.

By comparing current results with measurements we have previously obtained for mainstream and sidestream smoke using the Three Kings™ charcoal product, we find that the PAH residues in the unburned charcoal amount to 66% of the total PAH mass delivered in the combined sidestream and mainstream smoke, and 15% of the 5- and 6-ring PAH mass (Table 2). This demonstrates a potential for desorbed PAH residues to account for a significant part of the PAH delivered in the smoke, but not the entire balance. The data shown in Table 2 also indicate that the high naphthalene mass provided by the raw charcoal may facilitate the pyrosynthesis of higher molecular weight PAHs through a successive ring build-up mechanism (see Ledesma et al., 2002) during smoking.

4. CONCLUSIONS

Waterpipe charcoal products are abundant with PAH when purchased off the shelf. While we have previously learned that the burning charcoal releases large quantities of carcinogenic PAH into the mainstream and sidestream smoke of the narghile waterpipe, the current study demonstrates that charcoal products contain significant quantities of carcinogenic PAH even before they are lit, and that these residues may constitute a significant fraction of the PAH emitted by the charcoal. This study also demonstrates that these PAH residues vary widely and systematically by product. Taken together, these findings suggest that public health agencies following TobReg's recommendations should therefore move to regulate smoked charcoal products alongside tobacco.

Finally, the study also shows that charcoal products marketed as "environmentally friendly" and "natural" can contain more man-made carcinogens than products not marketed as such.

Acknowledgments

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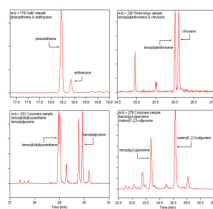
Figure 1.
SICP-chromatograms of various PAH identified in the three charcoal samples

Table 1

PAH residues in three types of waterpipe charcoal sampled in municipal Beirut. N = 3 samples for each charcoal product. Results expressed as mean(SEM).

PAH (ng/g charcoal)	Lump	Three Kings™	CocoNara™
Naphthalene	260(60)	770(120)	1680(350)
Acenaphthylene	5(1.0)	3(0.1)	250(72)
Acenaphthene	3(0.5)	2(0.1)	5(0.5)
Fluorene	20(2)	20(2)	45(8)
Phenanthrene	60(15)	120(9)	310(90)
Anthracene	14(3)	22(2)	67(18)
Fluoranthene	22(5)	69(5)	200(60)
Pyrene	26(5)	85(7)	170(52)
Benzo[a]anthracene	11(2)	20(2)	37(6)
Chrysene	11(2)	20(2)	38(6)
Benzo[b+k]fluoranthene	5(0.5)	10(1)	19(1)
Benzo[a]pyrene	8(0.9)	14(3)	18(1)
Benzo[g,h,i]perylene	5(0.8)	4(0.8)	8(0.9)
Dibenz[a,h]anthracene	1(0.1)	1(0.1)	3(0.4)
Indeno[1,2,3-cd]pyrene	4(0.7)	3(0.5)	7(0.6)
Total	455[***]	1163	2857[*]
Total excluding naphthalene	195[**,***]	393[*,***]	1177[*,**]
Sum of 5- and 6-ring PAH	23[***]	32[***]	55[*,**]

[*] indicates significant difference relative to lump charcoal,

[**] indicates significant difference relative to Three Kings™,

[***] indicates significant difference relative to CocoNara™.

Table 2

PAH emitted in combined mainstream (MS; see Sepetdjian et al., 2008) and sidestream smoke (SS; see Daher et al., 2010) and unburned charcoal from a narghile waterpipe smoked using 8.4 g of Three Kings™ charcoal.

PAH (ng per waterpipe)	In smoke (MS+SS)	In raw charcoal
Naphthalene[†]	2216	6470
Acenaphthylene	180	25
Acenaphthene	516	17
Fluorene	470	170
Phenanthrene	2707	1030
Anthracene	495	185
Fluoranthene	2476	580
Pyrene	2629	710
Chrysene+Benz[a]anthracene	880	340
Benzo[b+k]fluoranthenes	768	80
Benzo[a]pyrene	462	120
Benzo[g,h,i]perylene	406	34
Dibenzo[7a,h]anthracene	199	84
Indeno[1,2,3-c,d]pyrene	505	25
Sum of 5- and 6-ring PAH	2340	343
Total PAH	14909	9870

[†]Naphthalene is the only compound found in higher quantities in charcoal than in smoke