Analysis of Toxic Elements in Smoked Shisha Waterwaste and Unburnt Tobacco by Inductively Coupled Plasma-Mass Spectrometry: Probable Role in Environmental Contamination

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ABSTRACT
Shisha (also known as hookah, narghile or waterpipe) is a popular tobacco smoking device in South Asia and Middle East. Smoked shisha water, flavored (FSW) and non-flavored (NFSW) was analyzed for their environmental contamination potential using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Eighteen toxic elements were detected in the samples including arsenic, lead, cadmium, mercury and uranium. The levels of toxic elements were found to be higher in NFSW in comparison with FSW. Shisha tobacco, non-flavored (NFT) and flavored (FT), was also analyzed. Pattern of element levels in NFSW and FSW was similar with element levels in NFT and FT, respectively. Data indicate that the release of shisha water, either NSFW or FSW, into the environment may contribute to the accumulation of several toxic elements in soil and water. The present investigation provide a basis for further investigation of shisha water to assure whether regulatory measures are needed to handle this issue.

Key words: Shisha smoking, waste shisha water, tobacco, heavy metals, toxic elements, ICP-MS

INTRODUCTION
Tobacco smoking not just affects the human health, but it is also associated with the environmental contamination (Novotny et al., 2009; Novotny and Slaughter, 2014). Most of the environmental problems associated with the tobacco smoking have been attributed to the tobacco smoke itself, commonly regarded as Environmental Tobacco Smoke (ETS) (Matt et al., 2004; Kumar et al., 2015). However, several researchers have reported the environmental contamination by smoked cigarette butts (Novotny et al., 2009; Smith and Novotny, 2011). Several other smoking devices also need the attention of environmental monitoring studies. These devices include kretek, bidi and shisha (Lawrence and Collin, 2004; Panchamukhi et al., 2008; Dagaonkar and Udwadi, 2014).

Shisha (also known as ‘Hookah’, ‘Narghile’ or ‘Waterpipe’) is one of the popular smoking devices after cigarettes. It is smoked in several South Asian and Middle East countries, but has gained popularity among a number of western countries as well (Cobb et al., 2010; Martinasek et al., 2011; Maziak, 2011; Akl et al., 2015).

The present investigation focused on the analysis of water of the shisha devices which is usually believed to be a medium to filter out toxic substances from the tobacco smoke. The shisha water is discarded into drains after every smoking session of several minutes. The time of smoking session depends on the size of the shisha and the amount of the tobacco burnt. Charcoal is used to burn the tobacco using a clay head. Figure 1 depicts the basic outline and mechanism of shisha device.
Air contamination/pollution with several hundred chemicals released with tobacco smoke including polyaromatic hydrocarbons (PAHs), phenols, nitrosamines, formaldehyde, carbon monoxide, carbon dioxide etc.

Environmental Tobacco Smoke (ETS)

Exhaled

Inhaled

Tobacco and burning charcoal

Mainstream smoke

Side stream smoke

Shisha water containing soluble chemicals and heavy metals in tobacco smoke and trapped Tobacco Particulate Matter (TPM)

Discarded/released into the environment

Soil water contamination/pollution with several toxic tobacco smoke chemicals and heavy metals present in shisha water

Fig. 1: Shisha (also known as narghile, hookah or waterpipe) is not just a human health problem, but also contaminate the air by releasing smoke which is classified as Environmental Tobacco Smoke (ETS) and is a source of soil and water pollution by its water which is discarded after every smoking session.

The water used in the shisha ranges from 1-3 L in volume depending on the size of the shisha device. Fresh tap water is used for every new shisha smoking session. After smoking the water changes its color to pale yellow or brownish due to trapping of tobacco smoke particles and is replaced by fresh water for the next smoking session.

The shisha water, which is saturated with tobacco smoke tar and particles, has rarely been noticed for their environmental contaminating potential. In the present investigation, shisha water from flavored (FSW) and Non-Flavored Tobacco Smoke (NFSW) was analyzed for the toxic element content using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

MATERIALS AND METHODS

Chemicals and reagents: All the solvents, nitric acid, hydrogen peroxide and other reagents used were of highest purity grade. Flavored and non-flavored shisha tobacco was purchased from local market in Riyadh, KSA.

Shisha water collection: Shisha Water (SW) was collected from shisha lounges around Riyadh city. Two types of regularly smoked shisha tobacco (flavored and non-flavored) were targeted for
shisha water collection. Shisha water from different sessions was pooled and collected in 20 L plastic bottles. Bottles were properly washed with deionized water to avoid any contamination which might affect the results. Shisha water was filtered to remove charcoal debris. Collected samples were stored at room temperature and processed within 24 h after collection.

**Shisha water condensate:** To obtain the shisha, water condensate for the ICP-MS analysis, shisha water from flavored (FSW) and non-flavored (NFSW) smoked tobacco was kept in 2 L beakers on heating plates at 60°C. Moderate temperature was applied to avoid over drying and charring of the condensate. Beakers were left for 48 h on heating plate. When the condensate developed thicker, heating plate was switched off and condensate was collected in 25 mL beakers and left in a fuming hood to evaporate the remaining water content. Thus obtained dried condensate was stored at 4°C in airtight vials until further processing for ICP-MS analysis.

**Shisha water condensate preparation for analysis:** Dried condensate from FSW (0.496 g) and NFSW (0.618 g) and Flavored Tobacco (FT) and Non-Flavored Tobacco (NFT) (9.5 g each) were added into 50 mL of 20% Nitric acid (HNO₃) in a conical flask. The flask was kept on a heating plate at 85°C in a fuming hood for 48 h or until the complete digestion of the samples. During the digestion period the volume of the mixture was kept at the same level by intermittently adding 20% Nitric acid. After the samples (FSW, NFSW, FT and NFT) were completely digested by the 20% Nitric acid, the samples were filtered using Nalgene filter unit (Thermo scientifc). The filtrate was collected into a 100 mL volumetric flask and the volume was made up to 100 mL using deionized water (Milli Q), samples were analyzed by ICP-MS.

**Elemental analysis by ICP-MS:** FSW and NFSW were analyzed for the elemental constituents utilizing ICP-MS (ELAN-9000, Perkin Elmer, USA). Details of the instrumental settings are given below:

- RF power : 1500 watts
- Plasma gas flow : 15 L min⁻¹
- Auxiliary gas flow : 1 L min⁻¹
- Nebulizer gas flow : 0.83-0.88 L min⁻¹
- Peristaltic pump speed : 0.5 mL min⁻¹
- Nebulizer/spray chamber PFA-ST/peltier-cooled cyclonic
- Spray chamber temp : 2°C
- Detector mode dual lens/autolens enabled
- Sampler/skimmer cones nickel
- Scanning mode : Peak hopping
- Number of points/peak : 1
- Number of sweeps/reading : 10
- Number of readings/replicate : 1
- Number of replicates : 3

**ICP-MS calibration:** The ICP-MS instrument was calibrated using several standards of elements which include beryllium, lead, selenium, magnesium, rhodium, indium, cobalt, sodium, uranium, iron, copper and barium. To achieve the goal of calibration, 1000 ppm stock solutions (of each above
mentioned element) were used. Out of 1000 ppm stock solution, to make a working solution of 1 ppm the stock solution was subjected to serial dilution. The 10 ppm stock solution was made by adding 500 µL stock solutions of the each element to a 50 mL volumetric flask and making up the final volume to 50 mL by the addition of 1% HNO₃. This multi-element stock solution (10 ppm) was further diluted to 1 ppm by adding 1% HNO₃ and the resulting solution was designated as tuning solution. This tuning solution was used to measure all performance aspects of the instrument, including mass calibration, resolution, nebulizer gas flow, Auto Lens calibration and daily performance checks.

RESULTS

Total solid matter in shisha water: The average dried weight of pooled shishawater condensate from different samples was calculated to be 124 mg L⁻¹ of FSW and 159.5 mg L⁻¹ of NFSW.

Elemental constituents: A total of 18 elements were analyzed in all four samples (FSW, NFSW, FT and NFT) which were selected on the basis of their toxicological and environmental significance (Table 1 and 2). In NFSW and FSW iron was found to be in highest amount and the beryllium content was the lowest (Table 1). Nickel was detected only in FSW and FT (0.287 ng L⁻¹ and 3.638 ng g⁻¹, respectively). In NFT and FT iron and aluminum were found to be more abundant than any other element detected (Table 2). Mercury was found to be present in minute amount in all the samples. After the iron, zinc was the metal detected in highest amount in FSW and NFSW (Table 1). Arsenic, one of the most toxic elements, was found to be in high amounts in NFSW (39.087 ng L⁻¹), as compared with FSW (6.137 ng L⁻¹). Other toxic elements which were detected in high amount in NFSW, when compared with FSW, includes aluminum, vanadium, manganese, cobalt, selenium, silver, cadmium, antimony, barium, mercury and uranium. Lead was found to be present in fair amount in both the samples, slightly higher in FSW (FSW = 79.068 ng L⁻¹; NFSW = 71.742) (Table 2). When compared with element levels in NFT and FT (Table 2),

| Elements detected | Non-flavored shisha water (ng L⁻¹) | Flavored shisha water (ng L⁻¹) |
|-------------------|-----------------------------------|-------------------------------|
| Be                | 0.0193                            | 0.0125                        |
| Al                | 47.682                            | 25.200                        |
| V                 | 10.588                            | 6.625                         |
| Cr                | 8.620                             | 9.193                         |
| Mn                | 6.826                             | 1.762                         |
| Fe (µg L⁻¹)       | 28.719                            | 1.895                         |
| Co                | 3.839                             | 0.406                         |
| Ni                | 0.000                             | 0.287                         |
| Cu (µg L⁻¹)       | 15.883                            | 13.735                        |
| Zn                | 147.595                           | 108.081                       |
| As                | 39.087                            | 6.137                         |
| Se                | 25.931                            | 2.325                         |
| Ag                | 0.587                             | 0.081                         |
| Cd                | 3.697                             | 0.475                         |
| Sb                | 5.807                             | 0.256                         |
| Ba                | 92.570                            | 3.500                         |
| Hg                | 0.116                             | 0.0437                        |
| Pb                | 71.742                            | 79.068                        |
| U                 | 1.013                             | 0.306                         |

Be: Beryllium, Al: Aluminum, V: Vanadium, Cr: Chromium, Mn: Manganese, Fe: Iron, Co: Cobalt, Ni: Nickel, Cu: Copper, Zn: Zinc, As: Arsenic, Se: Selenium, Ag: Silver, Cd: Cadmium, Sb: Antimony, Ba: Barium, Hg: Mercury, Pb: Lead, U: Uranium
Table 2: Amount of toxic elements detected, in non-flavored and flavored shisha tobacco (Unburnt), by inductively coupled plasma mass spectrometry

| Elements detected | Amount detected except aluminum iron and manganese (ng g⁻¹) |
|-------------------|------------------------------------------------------------|
|                   | Non flavored tobacco (µg g⁻¹) | Flavored tobacco (µg g⁻¹) |
| Be                | 1.097                        | 0.0125                     |
| Al (µg g⁻¹)       | 18.461                       | 1.004                      |
| V                 | 53.421                       | 11.364                     |
| Cr                | 64.152                       | 23.240                     |
| Mn (µg g⁻¹)       | 1.701                        | 896.694                    |
| Fe (µg g⁻¹)       | 90.828                       | 8.504                      |
| Co                | 13.676                       | 2.356                      |
| Ni                | 0.000                        | 3.638                      |
| Zn                | 743.443                      | 257.866                    |
| As                | 22.286                       | 11.281                     |
| Se                | 16.237                       | 1.793                      |
| Ag                | 0.334                        | 0.010                      |
| Cd                | 3.615                        | 0.713                      |
| Sb                | 1.013                        | 0.354                      |
| Ba                | 840.779                      | 153.852                    |
| Hg                | 0.480                        | 0.041                      |
| Pb                | 41.510                       | 4.097                      |
| U                 | 1.807                        | 0.072                      |

Be: Beryllium, Al: Aluminum, V: Vanadium, Cr: Chromium, Mn: Manganese, Fe: Iron, Co: Cobalt, Ni: Nickel, Zn: Zinc, As: Arsenic, Se: Selenium, Ag: Silver, Cd: Cadmium, Sb: Antimony, Ba: Barium, Hg: Mercury, Pb: Lead, U: Uranium

NFSW and FSW show a similar pattern of element levels (Table 1). It indicates that the elements from tobacco are released in smoke and trapped into the water according to their amount in unburnt tobacco.

**DISCUSSION**

A significant number of publications have raised concern regarding human health and the environmental contamination by shisha smoking (Chaouachi, 2009; Aslam et al., 2014). None of the reports, searched in publication databases, found directly dealing with investigation of shisha water in terms of environmental pollution. The present study investigated the toxic elemental constituents in smoked shisha water in order to assess the role of the same in environmental contamination.

On the basis of ‘Priority List of Hazardous Substances’ given by Agency for Toxic Substances and Disease Registry (ATSDR., 2013) and ‘Priority Chemicals’ by Environmental Protection Agency (EPA), 18 elements were analyzed in the FSW, NFSW, NFT and FT. A fair amount of all the elements was detected in all of the samples (Table 1 and 2).

Various researchers consider shisha smoking as a global health problem (Maziak et al., 2015). A number of epidemiological studies have reported a correlation between shisha smoking and increasing number of the cancer (Maziak, 2013) and other diseases (Aslam et al., 2014). An increase in popularity of shisha smoking and consequent morbidities not only impose a public health problem, but also an increase in environmental contamination in terms of Environmental Tobacco Smoke (ETS) (Chaouachi, 2009) and waste materials including tobacco ash and shisha water. In the present study, we identified 18 elements in shisha water as well as in unburnt tobacco which are very well known to contaminate the environment and enter the food chain by means of bioaccumulation. Out of these 18 elements arsenic, lead, cadmium, mercury and uranium are the most toxic known to affect the human health (Jarup, 2003; Wirth and Mijal, 2010). Some of them, including manganese, iron, zinc and selenium are known to have biological functions, but at higher amount they are toxic (Rusyniak et al., 2010) and have potential to contaminate the environment.
Heavy metals not only impose health problems in humans and animals, they are also known to cause toxicity and physiochemical alterations in plants (Shahid et al., 2014). Accumulation of toxic elements in the soil and water of an ecosystem is a threat to fauna and flora flourishing in such a contaminated environment.

Results indicate that the elements in the shisha water are present according to their corresponding levels in the unburnt tobacco. This occurrence infers that the metals and non-metals are released with the smoke according to their concentration in the tobacco and get trapped/absorbed in low amount into the water with similar pattern. The amount of trapped elements may be low in shisha water, but the frequency of smoking, number of smokers, amount of tobacco, volume of water used in the shisha and accumulation tendency of the elements into the environment surely plays a crucial role in consideration of shisha water as an environmental problem.

Like cigarette smoke, shisha smoke also contains several toxic chemicals including furans (Schubert et al., 2012a), carbonyls (Schubert et al., 2012b) and polyaromatic hydrocarbons (PAHs) (Sepetdjian et al., 2008). Presence of these chemicals in shisha water along with heavy metals and metalloids further increases the environmental concern associated with it.

CONCLUSION
Based on the results it can be concluded that the shisha water from flavored and non-flavored tobacco contain toxic heavy metals and non-metals which along with other chemical constituents contaminate the water and soil. Unlike cigarette litter, shisha water cannot be recollected once it is released into the environment. Proper regulatory measures should be undertaken to avoid the environmental contamination by shisha water.

ACKNOWLEDGMENT
The special thanks are due to Research Center, College of Pharmacy, King Saud University, Riyadh, Kingdom of Saudi Arabia.

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