Evaluation of Polycyclic Aromatic hydrocarbons (PAHs) in webs of Eresid Spider from Punjab, Pakistan

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Abstract

This study was designed to assess the level of Polycyclic Aromatic Hydrocarbons (PAH) in Eresid spider webs and highlight its potential as air pollution indicator. To achieve the objectives, colonies of Eresid spiders were sampled during spring season from 22 different sites of Punjab, Pakistan. These spider webs were collected from variety of habitats including urban, industrial, agricultural and mixed area along the roads. The PAHs trapped in each spider web colony were extracted and quantitatively analyzed by a technique GCMS for 16 PAH compounds. The highest concentration (944.479 pg/g) of PAHs was recorded from Kalasha Kaku, whereas lowest concentration (140.122 pg/g) was recorded from Moutra, Sialkot. Among major congeners of PAH, Pyrene (61.42pg/g), Naphthalene (60.03pg/g), Fluoranthene (49.02pg/g), Benzo[a]anthracene (48.78pg/g) were analyzed in eresid spiders. Highest concentrations of PAH recorded from Industrial area followed by mixed area, urban and agricultural area. Overall high PAH concentrations in spider web were observed in industrial areas with high human activities. The results of the present study highlighted that Eresid spider web could be used in assesment of PAHs and other air pollutants

Key words: Polycyclic aromatic hydrocarbons, spider, webs, indicator, air pollution.

Introduction

PAHs are the air pollutants, which are mainly released from different human activities such as industrial, traffic, burning of fossil fuel and waste [1, 2]. When PAHs become the part of the atmosphere, it may disperse at longer distance through wind currents. The dispersion of PAH in the atmosphere depends upon different environmental factors viz; wind velocity, direction, ambient temperature, and relative humidity [3, 4, 5]. PAHs are one of the major group contaminants, possess mutagenic, teratogenic and carcinogenic properties. During the last two decades, scientists are focusing on the carcinogenic effects of PAH and some of them such as Anthracene, benzo(a)pyrene, chrysene, fluorene and pyrene are major chemical species of PAHs [7]. Human exposure to PAHs is also an increasing concern caused due to different abnormalities in infants such as growth retardation, developmental and memory defects [7]. Some PAH such as indeno [1,2,3,cd]pyrene, benzo[b]fluoranthene, benzo(a)pyrene, dibenzo[a,h]anthracene and benzo[k]fluoranthene have some carcinogenic effects. Therefore, monitoring the level of PAH in atmosphere is of the great importance, because of their noxious effects on human population may lead to defects and disorders [8]. Xiao-li et. al. [9] highlighted that spider web can be used to monitor the PAHs in air. The monitoring of PAH using spider web as an indicator is potentially operative, non-expensive and reliable [10,11]. The web of Eresid spider is thick, sticky and long lasting that can the trap the air born pollutants [11]. Therefore, the present study was designed to highlight the level of PAH in the web of Eresid spider collected from Punjab, Pakistan.

Materials and methods

The webs of *Stegodyphus sarasinorum* were collected from 22 localities situated in the Punjab, Pakistan during spring, 2015 (Figure 1) from diverse habitats with different level of human activities; urban, industrial, traffic, agricultural area. Five grams of spider web from the upper surface of the colony and dipped in 40 ml methanol-acetone (1:1, v/v) and shaked for one hour. After this, the extract was filtered and diluted and pH of the elute was adjusted at 2. The organic fractions separation and clean up were performed using solid phase extraction [13, 14]. The volume of final elute was reduced up to one ml under nitrogen stream and was sealed into small vials with the addition of standards. The quantitative analysis of PAH was performed using Gas Chromatography-Mass Spectrometry (GCMS) at State key Laboratories of Organic Geochemistry, Guangzhou Institute of Geochemistry, the Chinese Academy of Sciences, Guangzhou, People's Republic of China. Spatial distribution of PAHs was assessed and interpolated using Geographic Information System (GIS).

Results and Discussion

A total of Σ_{16}PAHs in spider web was analyzed from eresid spider webs from different localities of Punjab are given in Table 1. The highest concentration of Σ_{16}PAHs was observed in web collected from Kala shah Kaku (944.47pg/g) followed by Toba Tek Singh (634.74pg/g), Lalamusa (515.59pg/g), Rawat (506.19pg/g/) and minimum at Moutra, Sialkot (140.12 pg/g). The highest mean concentration of PAH was recorded in industrial area, followed by mixed urban and agricultural area. Significant difference of total PAH among industrial, mixed area, urban and agriculture was observed ($p = 0.05$). The highest concentration of Σ_{16}PAHs compounds in industrial area (461.466 pg/g), followed by urban area (416.252pg/g), a mixed area (275.443pg/g) and lowest concentration in agricultural area (271.794 pg/g) is shown in Figure 2.

Naphthalene, fluoranthene and Indeno{1,2,3,cd}pyrene concentration in spider web were observed highest in the industrial area as compared to the PAH web collected from other areas. Acenaphthylene and Phenanthrene concentrations in the agricultural areas were higher however with least contribution in the total PAHs. In mixed area, the level of pyrene, and Dibenzo{a,h}anthracene was recoded as compared to rest of the areas. The total PAHs concentration in the urban area was significantly lower than the rest of the zones (Figure 3). The PAHs concentrations in the spider webs were significantly high at industrial, urban and mixed human activities (Figure 4). The eresid spider colonies on the acacia tree along the exposed to the PAHs, pollutants and particulate matter. Due to physical properties of spider web, pollutants can stay for long time. Rybak and Olejniczak [11] reported that that spider webs have ability to immobilize polycyclic aromatic hydrocarbon compounds and retain it.

Several studies have been conducted for the assessment of PAHs and metals in spider webs, which highlighted the atmospheric deposition of PAH [11, 12, 15, 16]. PAHs detected in atmosphere of other countries showed high concentration level as compared to Pakistan shown in Table 2. Kamal et al., [17] reported 2023-2393pg/m^3 of PAHs from air of Lahore, Guranwala and Rawalpindi, Pakistan, whereas, spider webs collected from the same area showed the low level of deposition of PAHs. Similar findings were observed by Rybak and Olejniczak [11] high PAHs in spider webs from vehicle traffic, railway traffic, residential and municipal area. However, the PAH deposition level was quite high as observed by Rybak and Olejniczak [11] in comparison to the present study. Rybak and Olejniczak [11] documented that spider webs are the good indicators of traffic emission due to their ability to immobilize PAH compounds. This was the pioneer study; more experiments are required to assess the comprehensive record of PAHs deposition in spider webs resulted from anthropogenic activities.

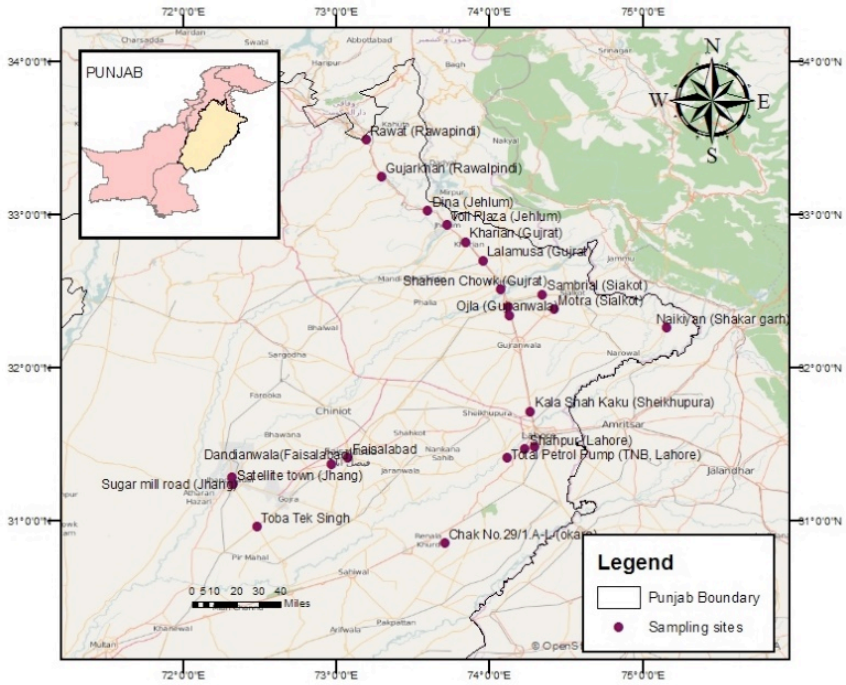

Figure 1: Map of study area showing the spider web sampling Sites in Punjab, Pakistan

Table 1: Basic statistics Mean ± SD, Median, Range (mini – Max) of different chemical species of PAH (pg/g) in Spider web.

S #	Variable	Mean ± SD.	Median	Min - Max
1	Nephthalene	59.84±30.49	62.36	3.63 - 105.64
2	Acenaphthene	4.32 ± 6.80	1.69	0.00 - 31.89
3	Acenaphthylene	3.64 ± 3.14	3.06	0.62 - 14.97
4	Fluorene	10.60 ± 17.56	3.70	0.00 - 78.28
5	Phenanthrene	25.81 ± 66.22	10.33	0.67 - 318.21
6	Anthracene	27.64 ± 45.18	7.06	0.47 - 150.88
7	Fluoranthene	49.02 ± 37.17	46.17	0.00 - 140.87
8	Pyrene	61.42 ± 42.29	50.14	0.00 - 192.02
9	Benzo(a)anthracene	48.78 ± 30.45	47.17	2.29 - 120.72
10	Chrysene	9.40 ± 11.49	5.13	0.62 - 44.99
11	Benzo(b)fluoranthene	5.82 ± 12.13	0.94	0.12 - 53.02
12	Benzo(k)fluoranthene	3.73 ± 3.83	2.39	0.00 - 14.68
13	Benzo(a)pyrene	1.74 ± 1.57	1.43	0.00 - 5.43
14	Indeno(1,2,3,c,d)pyrene	26.54 ± 98.14	2.67	0.23 - 464.31
15	Benzo(ghi)perylene	2.83 ± 4.11	1.35	0.00 - 15.74
16	Dibenzo(a,h)anthracene	9.28 ±16.76	3.52	0.00 - 79.01

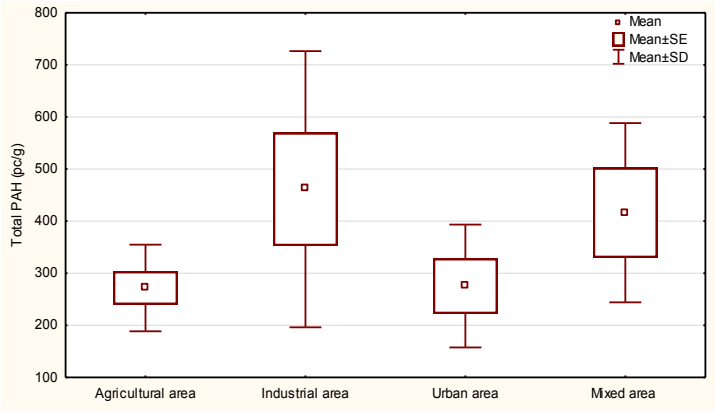

Figure 2: Distribution Pattern of PAHs (pg/g) in spider web in Urban, Agriculture, Industrial and Mixed Area

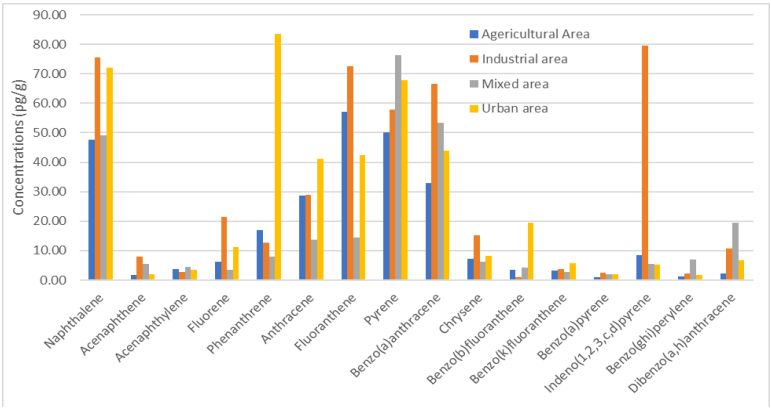

Figure 3: The concentration of each PAH compound (pg/g) in spider web from Urban, Agriculture, Industrial and Mixed Area.

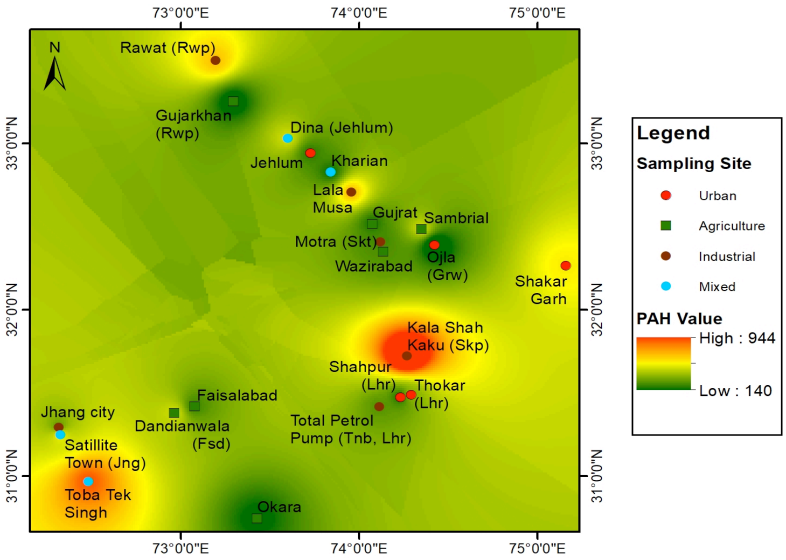

Figure 3: Spatial Distribution of PAH in Spider Web collected from different locations Punjab.

Table 2: Comparisons of PAHs in the present study with other global studies

Country	PAH	Area	PAH Concentration	Medium	References
Pakistan	16	Urban Agriculture Industrial Mixed	275.443 pg/g 271.794 pg/g 461.466 pg/g 416.252 pg/g	Eresid Web	Present study
Pakistan	16	Residential Industrial/Agriculture Industrial/Traffic	2023pg/m^3 2360 pg/m^3 2393 pg/m^3	Atmosphere	[17]
Poland		Surface Road Road Tunnel Railway Parking	1,859.1- 2,450.3 ng/g 5460.8 ng/g 3920.8 - 2027.34 ng/g 1,859.1- 2,450.3 ng/g	Spider web (dry deposition)	[11]
India	16	Industrial	72.7ng/m^3	Atmosphere	[18].
China	17	Urban	23.4 to 513 ng/m^3	Particulate matter	[21]
Korea	15	Urban	89.29ng/m^3	Atmosphere	[19]
Taiwan	21	Urban Rural Industrial	122 ng/m^3 79.1 ng/m^3 115 ng/m^3	Atmosphere	[20]

References:

[1]. Grynkiewicz, M., Polowska, Z. & Namiensik, J. (2002). *Atmosph. Env*., 36, 361-369.
[2]. Pandey, S. K., Kim, K. H., & Brown, R. J. (2011). *TrAC*, 30(11), 1716-1739.
[3]. Lima, ALC, Farrington JW & Reddy CM (2005). *Env. Forensics*, 6(2), 109-131.
[4]. Zhang, Y., & Tao, S. (2009). *Atmosph Env*. 43(4), 812-819.
[5]. Kural G, Çağlar Balkıs N, Aksu A. (2018). *IJEGEO*.;5(1):1-6.
[6]. Lv J, Xu R, Wu G, et al., (2009). *J. Env.Mon*.. 11(7):1368-74.
[7]. Perera FP, Rauh V, Whyatt RM, et al., (2005). *Neurotox*. 1;26(4):573-87.
[8]. Guo W, He M, Yang Z., et al., (2009). *J. of Hazard Mat.,* 164, 1379-1385.
[9]. Xiao-li, S., Yu, P., Hose, et a., (2006). *Bull. Environ. Contam. Toxicol*, 76, 271-277.
[10]. Rybak, J. (2014). *J.Ecol. Eng*., 15, 39-45.
[11]. Rybak J, Olejniczak T. (2014). *Environ. Sci. & Pollut. Res*., 1;21(3):2313-24.
[12]. Rybak, J., Sowka, I. & Zwozdziak, A (2012). Env. Prot. Eng. 38(3).
[13]. Niederer, M. (1998). *Environ. Sci. & Pollut. Res*., 5(4), 209-216.
[14]. Shirdam, R., Farahani, A., Khajavi, F. & Baghai, P. (2007). *Iran. J. Chem. Chem. Eng*., 26(2).
[15]. Hose GC, James JM, Gray MR (2002). Environ Pollut 120(3):725–733.
[16]. Ayedun H, Adewole A, Osinfade BG et al., (2013). *J Environ Chem Ecotoxicol* 5(2):21–25.
[17]. Kamal A, Malik RN, Martellini T et al., (2015). *Environ. Sci. & Pollut. Res*., 1;22(14):10580-91.
[18]. Singla V, Pachauri T, Satsangi A, et. al., (2012). *Polycyc. Arom. Compd*. 1;32(2):199-220.
[19]. Park, SS, Kim YJ, Kang CH (2002). *Atmos. Env*., 36 , pp. 2917-2924.
[20]. Fang GC, Chang KF, Lu C, Bai H. (2004). *Chemosph*. 1;55(6):787-96.
[21]. Shi J, Peng Y, Li W, et al., (2010). Aerosol Air Qual. Res. Oct 1;10(5):507-18.