

Original Article

Polycyclic Aromatic Hydrocarbons in Surface Soils

MUNTEAN Nicoleta¹, Edward MUNTEAN^{1*}, Livia ALHAFEZ², Marcel DUDA¹

*University of Agricultural Science and Veterinary Medicine Cluj-Napoca, Mănăştur Street, no. 3 - 5
400372 Cluj-Napoca, Romania
Babeş-Bolyai University, 30 Fantanele Street, 400294 Cluj Napoca, Romania*

Received 10 March 2013; received and revised form 29 March 2013; accepted 7 April 2013
Available online 1 June 2013

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants intensively studied mainly due to their widespread occurrence in environmental matrix, including surface soils. This study presents some preliminary results on assessment of PAHs contamination of surface soils originating from different locations in Transylvania, covering roadside, residential and agricultural areas. PAHs were determined by high performance liquid chromatography using an Agilent 1100 system with fluorescence detection, able to separate 14 PAHs: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene. This study proved that PAHs are part of the soil mixture, with total concentrations ranging from 0.09 to 81.40 µg/ kg, the highest recorded values being for chrysene (38.70 µg/ kg), pyrene (14.78 µg/ kg) and indeno(1,2,3-cd)pyrene (10.48 µg/ kg); the highest soil contamination was established for soil originating from Cluj Napoca city center (81.40 µg/ kg).

Keywords: polycyclic aromatic hydrocarbons, PAH, HPLC, soil, pollution.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic molecules with two or more fused benzene rings (fig. 1), with great environmental concern as they are among the most widespread organic pollutants. Their wide environmental occurrence is due to both natural causes (such as volcanic activity or incomplete combustions in forest fires) or anthropogenic ones (incomplete combustion of fossil fuels and other organic substances, petroleum refineries, industrial processes, vehicle's exhaust) [6, 7, 14]. Low molecular mass PAHs are mostly found in the gas phase while the heavier ones are mainly associated with airborne particles; PAHs also occur in high amounts in crude oil, coal, and tar deposits.

As pollutants, they are of concern because some compounds have been identified as carcinogenic, mutagenic and teratogenic. PAHs contaminates the soils mainly through atmospheric deposition [10], sequestration being afterwards the major mechanism for their accumulation [15], the factors that influence levels of PAHs in surface soils being the distance from point sources, climatic conditions and soil organic matter [5, 13]. Once entered in the soil matrix they accumulate in horizons rich in organic matter where they are likely to be retained due to their persistence and hydrophobicity; afterwards, PAHs can be subjected in time to various transformations as an effect of volatilization, photo-oxidation, chemical oxidation or leaching [4, 9, 15]. PAHs contaminates the soils mainly through atmospheric deposition [10], sequestration being afterwards the major mechanism for their accumulation [15], the factors that influence levels of PAHs in surface soils being the distance from point sources, climatic conditions and soil organic matter [5, 13].

*Corresponding author
tel +40754074375; fax +40264593792
e-mail: edimuntean@yahoo.com

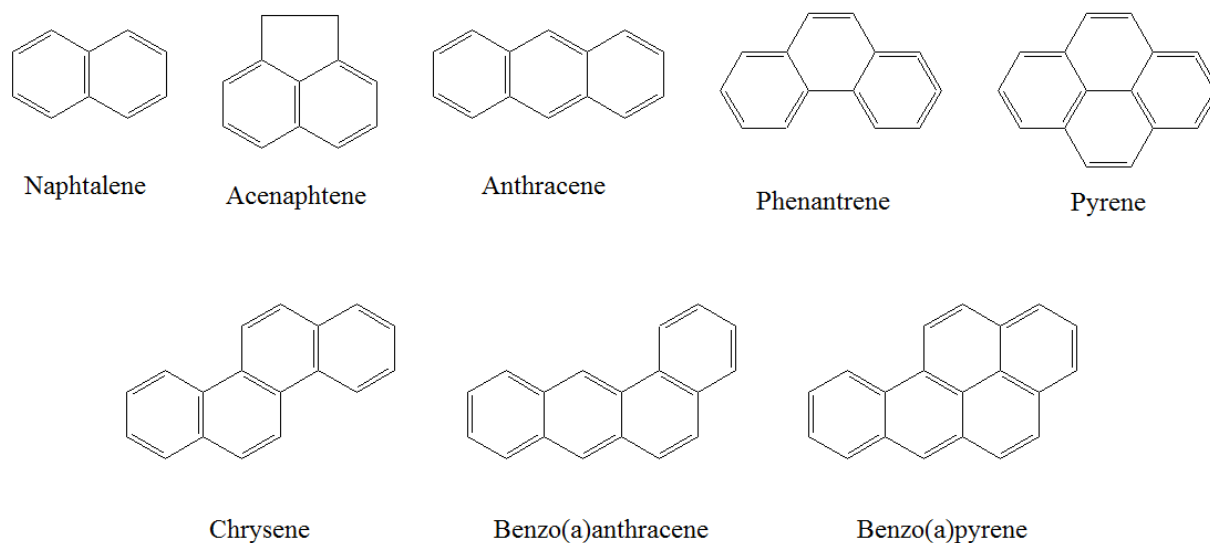


Figure 1. Structures of some polycyclic aromatic hydrocarbons

Once entered in the soil matrix they accumulate in horizons rich in organic matter where they are likely to be retained due to their persistence and hydrophobicity; afterwards, PAHs can be subjected in time to various transformations as an effect of volatilization, photo-oxidation, chemical oxidation or leaching [4, 9, 15].

The detection of PAHs in surface soil is important for environmental investigations, because soil system is a major collector for PAHs due to its high surface and holding capacity for organic pollutants, being also a good indicator of environmental pollution and environment risk for human exposure [7, 14]. As the PAHs' impact on environment is complex, these substances gained an increased attention by a wide research community; different levels of soil contamination with PAHs have been reported, both high ones in industrialized areas [1, 8, 11, 12] and low ones [3, 15, 16]. PAHs present in soil not only create a risk to humans through food chain contamination, but they may also exhibit a toxic activity on plants and microorganisms.

This study evaluates PAHs from three sites: one urban (Cluj Napoca) and two rural (Jucu and Seica Mare), the major objective being to determine the level of PAHs contamination in different environmental conditions. Cluj-Napoca is a city situated in the Western part of Transylvania's Depression, along the river Someş; the city is moderately industrial but has heavy traffic. Seica Mare is a small community in Romania, situated at a distance of 14 km to Copsa Mica (a highly polluted town for many years, being classified in 2008 as a "environmental disaster area"); Jucu is a village situated at 18 km east from Cluj Napoca, in an

unpolluted area. The sampling sites were selected both on cultivated and non-cultivated surfaces.

2. Material and Methods

Soil samples were collected in triplicate from the soil surface (0-10 cm), in polyethylene bags. The selected sampling sites cover roadside, residential and agricultural areas:

- site 1. Jucu (46°52'15.07" N 23°45'32.34" E) – cultivated area, reference unpolluted site
- site 2. Seica Mare (46°01'50.47" N 24°09'38.13" E) – cultivated area
- site 3. Cluj Napoca (46°45'56.82" N 23°34'00.70" E) – cultivated area (private garden)
- site 4. Cluj Napoca (46°45'31.64" N 23°32'59.69"E) – close to a gas station
- site 5. Cluj Napoca (46°46'12.65" N 23°35'23.30" E) – city center
- site 6. Cluj Napoca (46°44'56.29" N 23°32'20.29" E) - wood – burning area

The samples were labeled, sealed and transported to the laboratory where they were crushed, mixed and cleaned from extraneous material, then average samples of ~20 g soil were weighed, placed in beakers together with 100 mL hexane; the beakers were placed in a sonication bath for 30 minutes, then the obtained extracts were filtered, dried with sodium sulfate and concentrated to dryness in a rotary evaporator. Finally, the residues were dissolved in 1.5 mL acetonitrile and subjected to high performance liquid chromatographic (HPLC) analysis.

PAHs were purchased from Supelco (Bellefonte, PA, USA) as a TCL PAHs Mix at concentration of 20-1000 µg/mL in acetonitrile:methanol (90:10). Calibration solutions were prepared daily by diluting the standard solution with acetonitrile. Solvents used were all HPLC grade, being supplied by Merck (Darmstadt, Germany). Ultrapure water was obtained from a WATEK IWA 20 water purification system.

PAHs were determined by an Agilent 1100 high performance liquid chromatograph consisting in a solvent degasser, a quaternary pumping system, an autosampler, a column oven, a diode-array detector and a fluorescence detector. Separations were accomplished using an Envirosep PP column (125mm x 4.6mm I.D) using acetonitrile: water as mobile phase [1]. The applied HPLC method is able to quantify 14 PAHs: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo(a)pyrene and benzo(ghi)perylene. The quantitative analysis was accomplished by the

external standard calibration method; PAHs' identification was performed by comparison of their retention time with those of authentic standards. For peak identity confirmation, the diode-array detector's spectra were compared with reference compounds spectrum in the spectrum library. The procedure been checked for recovery efficiencies using spiked PAH samples; recoveries ranged between 27% and 83% and the reported data are corrected accordingly, considering the means of triplicate determinations. Data processing was accomplished using Chemstation 08.03 Software. Detection limit was 0.001 g/kg, with good linearities achieved for all PAHs, with correlation coefficients higher than 0.998.

3. Results and Discussions

The obtained results are summarized in table 1; the average concentration of total PAHs from the analyzed samples was in the range from 0.09 µg/ kg (Jucu) to 81.40 µg/ kg (Cluj Napoca – city center).

Table 1. Average concentrations of the determined PAHs [µg/ kg]

PAHs	Site 1 (Jucu)	Site 2 (Seica Mare)	Site 3 (Cluj Napoca garden)	Site 4 (Cluj Napoca gas station)	Site 5 (Cluj Napoca City center)	Site 6 (Cluj Napoca wood burning area)
Naphthalene	N.D.	N.D.	N.D.	0.02	N.D.	N.D.
Acenaphthene	N.D.	N.D.	N.D.	N.D.	9.59	0.05
Fluorene	N.D.	0.96	N.D.	0.01	0.98	0.04
Phenanthrene	N.D.	0.74	N.D.	N.D.	N.D.	N.D.
Anthracene	0.01	0.02	0.03	N.D.	0.40	N.D.
Pyrene	N.D.	N.D.	0.17	0.01	14.78	0.51
Benz(a)anthracene	0.03	0.18	0.05	0.26	0.75	0.85
Chrysene	N.D.	N.D.	0.11	0.20	38.70	1.45
Benzo(b)fluoranthene	0.02	0.17	0.34	0.35	3.40	0.14
Benzo(k)fluoranthene	N.D.	N.D.	0.05	0.10	0.51	0.08
Benzo(a)pyrene	N.D.	0.18	N.D.	N.D.	N.D.	N.D.
Dibenzo(a,h)anthracene	N.D.	0.02	0.68	0.71	1.59	0.53
Benzo(g,h,i)perylene	0.01	0.18	0.53	N.D.	0.72	3.76
Indeno(1,2,3-c,d)pyrene	N.D.	0.13	0.18	0.72	10.48	0.53
Total/ site	0.09	2.58	2.14	2.38	81.40	7.94

N.D. – not detected

From the 14 studied PAHs, naphthalene was detected only in the gas station area in a very small concentration (0.02 µg/ kg), while benzo (a) pyrene and phenanthrene only in Seica Mare (0.18 µg/ kg and 0.74 µg/ kg). The most contaminated site with PAHs was the one located in the Cluj Napoca city center: here the maximum PAHs concentrations were recorded, such as for chrysene (38.70 µg/kg), pyrene (14.78 µg/ kg), indeno (1, 2, 3-c, d) pyrene (10.48 µg/kg) and acenaphthene (9.59 µg/ kg). These data can be considered as a result of higher

emission rates in the central area; however, because the city center also receive emission for longer time, the observed high levels of PAHs may also be a result of the long term accumulation of these compounds in that area. Benzo (g, h, i) perylene had the higher concentration in the wood burning area (3.76 µg/ kg), this area having also the highest concentration of benz (a) anthracene (0.85 µg/ kg). In the gas station area, the most abundant proved to be indeno(1,2,3-c,d)pyrene (0.72 µg/kg),

dibenzo(a,h)anthracene (0.71 µg/ kg) and benzo(b)fluoranthene (0.35 µg/ kg).

High molecular mass PAHs are the most abundant ones in the studied soils, indicating older pollution, since the lighter PAHs are more biodegradable and are not expected to persist or be sorbed as strongly as the heavier PAHs. Due to different persistency, PAHs with different molecular weights exhibit different accumulation behaviors in soils; heavy molecular PAHs, with low vapor pressure and high resistance to degradation processes, actually exhibit strong accumulation, while low molecular weight PAHs can be volatilized and/or degraded leading to losses during their existence in soils.

4. Conclusions

This study proved that PAHs are part of the soil mixture, with total concentrations ranging from 0.09 to 81.40 µg/ kg, the highest recorded values being for chrysene (38.70 µg/ kg), pyrene (14.78 µg/ kg) and indeno(1,2,3-cd)pyrene (10.48 µg/ kg); the highest soil contamination was established for urban soil originating from Cluj Napoca's center (81.40 µg/ kg), while the lowest one proved to be in a rural agricultural area (Jucu - 0.09 µg/ kg).

References

- [1] Alhafez L., N. Muntean, E. Muntean, T. Mihaiescu, R. Mihaiescu, D. Ristoiu, 2012, Polycyclic aromatic hydrocarbons in wastewater sewerage system from the Cluj-Napoca area, *Environmental Engineering & Management Journal*, 11 (1), 5-12
- [2] Brandli T. C., T. Hartnik, T. Henriksen, G. Cornelissen, 2008, Sorption of native polyaromatic hydrocarbons (PAH) to black carbon and amended activated carbon in soil. *Chemosphere* 73, 1805–1810
- [3] Chung M. K., R. Hu, K. C. Cheung, M. H. Wong, 2007, Pollutants in Hong Kong soils: polycyclic aromatic hydrocarbons. *Chemosphere* 67, 464–473
- [4] Dean J. R., G. Xiong, 2000, Extraction of organic pollutants from environmental matrices: selection of extraction technique, *TrAC Trends in Analytical Chemistry*, 19 (9), 553–564
- [5] Hao R., H. F. Wan, Y. T. Song, H. Jiang, S. L. Peng, 2007, Polycyclic Aromatic Hydrocarbons in Agricultural Soils of the Southern Subtropics, China, *Pedosphere*, 17 (5), 673–680
- [6] Henner P., M. Schiavon, J. Morel, E. Lichtfouse, 1997, Polycyclic aromatic hydrocarbons (PAH) occurrence and remediation methods, *Analisis Magazine* 25 (9-10), M56-M59
- [7] Jiang Y. F., X. T. Wang, F. Wang, Y. Jia, M. H. Wu, G. Y. Sheng, J. M. Fu, 2009, Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China, *Chemosphere*. 75(8), 1112-1118
- [8] Mielke H. W., G. Wang, C. R. Gonzales, B. Le, V. N. Quach, P. W. Mielke, 2001, PAH and metal mixtures in New Orleans soils and sediments. *Science of the Total Environment*, 281, 217–227
- [9] Nam J. J., G. O. Thomas, F. M. Jaward, E. Steinnes, O. Gustafsson, K. C. Jones, 2008, PAHs in background soils from Western Europe: influence of atmospheric deposition and soil organic matter. *Chemosphere* 70 (9), 1596-1602
- [10] Pepin G. H. Baroudi, M. Nomine, 2003. Characterization of the pollutant-matrix interaction in contaminated soils: PAH and PCB contamination case study, *Management of Environmental Quality: An International Journal*, 14 (2), 293 – 300
- [11] Tang L., X. Y. Tang, Y. G. Zhu, M. H. Zheng, Q. L. Miao, 2005, Contamination of Polycyclic aromatic hydrocarbons (PAHs) in urban soils in Beijing, China, *Environment International*, 31, 822–828
- [12] Wang Z., J. W. Chen, X. L. Qiao, 2007, Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: a case study in Dalian, China, *Chemosphere* 68, 965–971
- [13] Wcislo E., 1998, Soil Contamination with Polycyclic Aromatic, Hydrocarbons (PAHs) in Poland - a Review, *Polish Journal of Environmental Studies*, 7 (5), 267-272
- [14] Wild S. R., K. C. Jones, 1995, Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget, *Environmental Pollution*, 88, 91–108
- [15] Yang Y., S. Tao, N. Zhang, D. Y. Zhang, X. Q. Li, 2010, The effect of soil organic matter on fate of polycyclic aromatic hydrocarbons in soil: a microcosm study, *Environmental Pollution*, 158 (5), 1768-74
- [16] Yang Y., X. X. Zhang, T. Korenaga, 2002, Distribution of polynuclear aromatic hydrocarbons (PAHs) in the soil of Tokushima, Japan, *Water, Air & Soil Pollution*, 138, 51–60