

EVALUATION OF METALS AND PAH (POLYCYCLIC AROMATIC HYDROCARBONS) CONTAMINATION LEVEL FROM CLUJ-NAPOCA SOIL

Tanaselia C., A. Becze, O. Cadar, M. Roman, D. Simedru*

*INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, 400293 Cluj-Napoca, Romania, *Corresponding author: dorina.simedru@icia.ro*

Abstract. Four soil samples (3 from the city exits and one from the Central Park) from Cluj-Napoca were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and High Performance Liquid Chromatography (HPLC) techniques to establish their level of contamination with metals and polycyclic aromatic hydrocarbons (PAH). The results for metal analysis obtained by ICP-MS showed a contamination of all investigated samples with Ni and As above the normal limits foreseen by Romanian legislation. Also one of the sample presented contamination with Mn above the normal limits. The results for PAH obtained by HPLC show a small contamination with naphthalene, phenanthrene and total PAH in the west exit of Cluj-Napoca. These results suggest that a further investigation of the soil from Cluj-Napoca it is necessary before drawing final conclusions.

Keyword: Soil, PAH, metals, HPLC, ICP-MS

INTRODUCTION

Elevated heavy metals content in soil can have two origins, geochemical background of the area or anthropogenic activity, the last one having the predominant proportion. A study of the United Nations [1] showed that in 2014 more than 3.8 billion people (more than half of world's total population) lived in urban areas. This impact both, the environment around such densely populated areas and citizen's health on the long term if the urban soil is contaminated with heavy metals from industrialization activities and urbanization. Soil contamination plays an important role in human health: it collects the contaminants resulting from human industrial activity [2, 3], especially in urban areas [4] and, in the same time acts, as a buffer that could influence the transport of heavy metals in other mediums: atmosphere, hydrosphere or vegetation. By transferring the pollutant agents, it indirectly impacts human health in a negative way [5, 6]. In general, human population is exposed to heavy metals by ingestion (food or drinks) or inhalation [7]. Vast majority of non-essentials heavy metals could have irreversible effect on human health and high concentration could lead to cancer or cause death. This is usually caused by heavy elements entering the body and act as a pseudo-element, mimicking the role of essential elements, thus interfering and disrupting natural metabolic processes [7].

Besides the metal pollution encountered in urban areas, another group of pollutants, namely polycyclic aromatic hydrocarbons (PAH) was taken in consideration. Polycyclic aromatic hydrocarbons (PAHs) are a large group of chemical contaminants [8] with properties negatively impacting the human organism such as carcinogenicity, mutagenicity, etc. [9]. These compounds are strongly hydrophobic and lipophilic as well as having a

propensity to accumulate in plant and animal tissues [10]. PAHs have also been shown to be partitioned or incorporated more or less reversibly into the humic substances of the soil after partial degradation and thereby be even more immobilised in the soil [11]. There are several possible sources of PAHs in the environment but the petrogenic and pyrolytic sources are considered to be the most important [10].

Due to its long industrial history, the continuously assessment of heavy metal and polycyclic aromatic hydrocarbons (PAH) contamination in Cluj-Napoca, the second largest city in Romania from population level point of view, is an important action for assuring safety levels of these contaminants. This study is proposing to determine the current situation of Cluj-Napoca regarding the pollutants mentioned above (metals and PAH).

MATERIAL AND METHODS

Sampling. In order to achieve the proposed purpose, several soil samples were taken from three exits of Cluj-Napoca, Romania and one from the central park of the city (Table 1).

Table 1

Sampling location	
Sample name	Location
Sample 1	West exit
Sample 2	East exit
Sample 3	South exit
Sample 4	Central Park

Reagents and standards

Metals. Analytical grade HNO₃ 65%, HCl 37% and ICP multi-element standard IV (1000 mg/L of Ca, Cu, Fe, Mn, Mg, Na, K and Zn in 0.2% (v/v) HNO₃) were purchased from Merck (Darmstadt, Germany). All dilutions were prepared using ultrapure water (18.2 MΩ/cm) obtained from a Millipore Direct-Q3 UV system (Millipore, France) was used.

PAH. PAH Calibration Mix containing 10μg/ml of each compound (Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Dibenz[a,h]anthracene, Benzo[ghi]perylene, Indeno[1,2,3-cd]pyrene) in Acetonitrile was acquired from Supelco. Hexane for HPLC (purity ≥99.9) was acquired from Sigma – Aldrich, Florisil (Merck) was used after heating overnight at 120°C. 0,45 μm filtration cartridge for syringe where acquired from Phenomenex, Ultra pure water obtained using Ultraclear TWF UV UF T from Evoqua Water Technology - Siemens.

Extraction method

Metals. The soil sample is first dried, then crushed to obtain particle under 150μm. 20 g of sample is extracted with a mix of HCl and HNO₃ then kept 16 hours at room temperature, followed by a reflux boiling for 2 hours. The extract is cleared and brought to volume with HNO₃. **PAH.** 10 g of homogenized and dry samples was extracted using 25 ml hexane in an ultrasonic bath for 60 min. The supernatant was purified on a Florisil clown and then evaporated to dry in a stream of nitrogen. The sample was reconstituted using 1 ml

of acetonitrile. For recovery study a 10 g of soil sample was spiked with 1 ml standard solution containing all the 15 PAH's in a concentration of 50 μ g/ml dissolved in acetonitrile. In the same time a blank sample from the same soil sample was analysed in order to correctly calculate the recovery.

Analytical methods

PAH. Liquid chromatography conditions. The method was developed using a Perkin Elmer 200 Series High Performance Liquid Chromatograph (HPLC) with FLD detector. System Parameters: Flow Rate: 1.4 ml/min, Gradient mobile phase of H₂O and Acetonitrile, Column Temp: 24°C, Injection Volume: 50 μ L, Column: INERTSIL ODS-P 5 μ m 15cm X 0.46cm, TEKNOKROMA, different wavelengths appropriate for each compound for the FLD detector. **Metals.** Inductively coupled plasma mass spectrometry (Elan DRC II instrument, Perkin-Elmer, Canada) was used for determining elemental composition of samples. A quantitative method was used for As, Cd, Cd, Cr, Co, Cu, Mn, Zn, Pb and Hg determination, while a semi-quantitative method for other elements was used. For the quantitative method, a calibration curve was developed (10 μ g/L, 20 μ g/L, 50 μ g/L and 100 μ g/L). If sample concentration exceeded the highest point on the calibration curve, the sample was properly diluted. Semi-quantitative method used response factor calibration curve for proper calibration before analysis. All the calibration procedures were performed before each sample batch. Elan DRC II parameters are listed in Table 2.

Table 2

Elan DRC II main parameters

Parameter	Value
Plasma	
Power / W	1400
Plasma gas flow / l min ⁻¹	15.00
Auxiliary gas flow / l min ⁻¹	1.10
Nebuliser gas flow / l min ⁻¹	0.89
Sample uptake rate / ml min ⁻¹	0.4
Quadrupole	
Quadruple rod offset (QRO) / V	0.00
Cell rod offset (CRO) / V	- 8.00
Cellpath voltage (CPV) / V	- 20.00
Measurement mode	Peak hopping
Dwell time / ms	200
Integration time / ms	4000
Reading per point	20
Reading per replicate	1
Replicate measurements	5

RESULTS AND DISCUSSIONS

Metals. The results obtained for metals analysis are reported in Table 3.

Table 3

Results obtained for metals in soil sample

No.	Name of compound	Sample 1 (mg/kg)	Sample 2 (mg/kg)	Sample 3 (mg/kg)	Sample 4 (mg/kg)
1.	Li	22.18	22.90	20.56	23.40
2.	Na	186.23	107.72	52.86	199.29
3.	Mg	5816.15	4223.35	2573.62	3643.19
4.	K	3748.59	2197.72	1616.20	1464.25
5.	Sc	5.60	3.89	3.75	3.84
6.	Ti	140.49	401.23	96.85	124.68
7.	V	45.04	31.36	28.42	31.17
8.	Cr	29.13	25.91	24.21	27.29
9.	Mn	541.89	423.46	633.67	1175.90
10.	Fe	18070.09	14367.67	14380.70	21375.48
11.	Co	8.96	7.61	9.57	10.78
12.	Ni	38.23	21.25	22.37	21.09
13.	Cu	13.88	13.55	13.17	12.14
14.	Zn	26.69	29.17	28.18	24.25
15.	Ga	8.12	5.17	5.17	4.85
16.	As	10.00	10.71	8.08	15.80
17.	Rb	40.67	25.62	22.04	21.47
18.	Sr	103.18	44.36	35.45	35.44
19.	Cd	0.13	0.11	0.14	0.11
20.	Sn	0.90	1.11	1.50	1.61
21.	Sb	0.29	0.33	0.26	0.31
22.	Cs	1.40	1.76	0.79	1.38
23.	Ba	138.90	93.05	99.11	163.35
24.	La	16.37	20.44	15.53	18.18
25.	Ce	41.84	50.24	40.24	45.08
26.	Hg	<LOD	0.04	0.04	<LOD
27.	Tl	0.22	0.21	0.17	0.19
28.	Pb	10.12	9.71	14.39	10.29
29.	Bi	0.12	0.22	0.15	0.21

*LOD = 0.03 mg/kg

According to The Minister Order 184 from 1997, it can be observed that all four samples exceed the normal value for Ni (<20 mg/kg) and As (<5 mg/kg) and the sample for the Central Park exceed also the normal limit for Mn (<900 mg/kg).

PAH. The results obtained for PAH analysis from investigated soil samples are presented in Table 4.

Table 4

Results obtained for soil sample

No.	Name of compound	Recovery (%)	Sample 1 (mg/kg)	Sample 2 (mg/kg)	Sample 3 (mg/kg)	Sample 4 (mg/kg)
1.	Naphthalene	74.1	0.0368	0.0013	0.0004	0.0063
2.	Acenaphthene	73.2	0.0235	0.0041	0.0006	0.0056
3.	Fluorene	74.9	0.0301	0.0176	0.0008	0.0047
4.	Phenanthrene	75.0	0.1169	0.0032	0.0084	0.0312
5.	Anthracene	73.0	0.0010	<LQ	0.0024	<LQ
6.	Fluoranthene	70.0	<LQ	<LQ	<LQ	<LQ
7.	Pyrene	81.9	0.0003	0.0004	<LQ	0.0001
8.	Benz[a]anthracene	74.3	<LQ	<LQ	<LQ	<LQ
9.	Chrysene	79.1	<LQ	<LQ	<LQ	<LQ
10.	Benzo[b]fluoranthene	73.4	<LQ	<LQ	<LQ	<LQ
11.	Benzo[k]fluoranthene	78.3	<LQ	0.0002	<LQ	<LQ
12.	Benzo[a]pyrene	76.3	<LQ	<LQ	<LQ	<LQ
13.	Dibenz[a,h]anthracene	77,6	<LQ	0.0002	<LQ	<LQ
14.	Benzo[ghi]perylene	75.9	<LQ	0.0001	<LQ	<LQ
15.	Indeno[1,2,3-cd]pyrene	74.3	<LQ	<LQ	<LQ	<LQ
16.	PAH TOTAL	-	0.2086	0.0272	0.0127	0.0479

*LQ = 0.00005 mg/kg

According to The Minister Order 184 from 1997, the PAH values for samples 2-4 are normal limits (<0.05 mg/kg). For sample 1 the values for naphthalene, phenanthrene and total PAH are little higher than the normal limits. The normal limit for naphthalene is <0.02 mg/kg, for phenanthrene is <0.05 mg/kg and for total PAH is <0.1mg/kg. The exceeding of the normal values can be associated with the increase traffic in that area. Figure 1 presents the main PAH compounds found in the soil samples are presented.

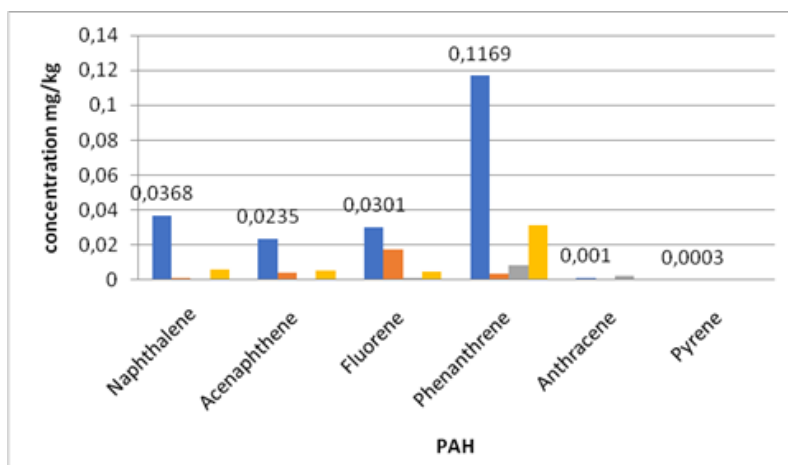


Fig. 1. Main PAH compounds found in the samples

CONCLUSIONS

The results obtained for analyzed soil samples from Cluj-Napoca show a small contamination with PAH in the west exit of Cluj-Napoca. Analyzing the metals results another contamination may be observed with Ni and As for all three exits and Central Park samples and also a contamination with Mn of the Central Park soil. These results suggest that a further investigation of the soil from Cluj-Napoca it is necessary before drawing final conclusions.

**All authors had equal contribution to this study.*

REFERENCES

1. United Nations (UN), World Urbanization Prospects, United Nations Department of Economic and Social Affairs/Population Division, Washington, DC (2014).
2. Yang, W., Wei, B., Yang, L., (2010), A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China, *Microchemical Journal*, 94 (2) : 99–107.
3. Gleyzes, C., Tellier, S., Astruc, M., (2002), Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures, *Trends in Analytical Chemistry*, 21 (6–7) : 451–457.
4. Sun, F.F. , Wang, F.H., Wang, X. , He, W., Wen, D.A., Wang, Q.F., Liu, X.X. , (2013), Soil threshold values of total and available cadmium for vegetable growing based on field data in Guangdong province, South China, *Journal of the Science of Food and Agriculture*, 93:1967–1973.
5. Mehr, M.R., Keshavarzi, B., Moore, F., Sharifi, R., Lahijanzadeh, A., Kermani, M., (2017), Distribution, source identification and health risk assessment of soil heavy metals in urban areas of Isfahan province, Iran, *Journal of African Earth Sciences*, 132: 16-26.
6. Kabata-Pendias, A., Pendias, H., (2001), *Trace Elements in Soils and Plants*, CRC Press, New York 2001.
7. Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B.B., (2014), Toxicity, mechanism and health effects of some heavy metals, *Interdisciplinary Toxicology*, 7 (2) : 60-72.
8. Zelinkova, Z., Wenzl T., (2015), EU marker polycyclic aromatic hydrocarbons in food supplements: analytical approach and occurrence, *Food Additives & Contaminants: Part A*, 32(11) :1914–192.
9. Ramesh, A., Walker, S.A., Hood, D.B., Guillen, M.D., Schneider, K., Weyand, E.H., (2004), Bioavailability and risk assessment of orally ingested polycyclic aromatic hydrocarbons. *International Journal of Toxicology* 23: 301-333.
10. Vane, C.H., Kim, A.W., Beriro, D.J., Cave, M.R., Knights, K., Moss-Hayes, V., Nathanail, P.C., (2014) Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK, *Applied Geochemistry* 51: 303–314.
11. Kästner, M., Streibich, S., Beyrer, M, Richnow, H,H, Fritsche, W., (1999) Formation of bound residues during microbial degradation of [14C]Anthracene in soil. *Applied and Environmental Microbiology* 65(5):1834-1842.