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Identification and Quantification of Polycyclic Aromatic Hydrocarbons in Soil from the Vinča Landfill (Serbia)

Mitić, J.[1,*], Kojić, I.[2], Relić, D.[3], Popović, A.[3], Milićević, T.[1]

[1]University of Belgrade, Institute of Physics Belgrade, National Institute of the Republic of Serbia, Pregrevica 118, 11080 Belgrade, Serbia

[2] University of Belgrade, Innovative Centre of the Faculty of Chemistry, Studentski trg 12–16, Belgrade, Serbia

[3] University of Belgrade, Faculty of Chemistry, Studentski trg 12–16, Belgrade, Serbia

*corresponding author:
e-mail: jelenadj@ipb.ac.rs

Abstract

Vinča landfill, the biggest sanitary landfill in Serbia, causes many environmental implications. The investigation of polycyclic aromatic hydrocarbons (PAHs) is of main importance due to the frequent landfill burning. In this study, eight soil samples (<630μm) from *Vinča* landfill were analysed using gas chromatography coupled with mass spectrometry (GC-MS) to determine the PAH concentrations in the soil. The PAH concentrations varied significantly across the samples, reflecting the differences in their respective environments. The range of PAH concentrations is 3.09E-05−2.15E-02 mg/kg. All 16 PAHs were identified in the samples, although naphthalene, acenaphthene, and fluorene were detected only in trace amounts. The plot of Ant/(Ant + Ph) versus Flu/(Flu + Py) ratios indicated that the PAHs mostly originate from petrogenic sources as well as biomass and coal combustion.

Keywords: landfill, PAH, soil, waste, origin.

1. Introduction

Vinča landfill is a municipal sanitary landfill (44.786531, 20.596590) of Belgrade (capital of Serbia). As the biggest sanitary landfill, it causes many environmental implications. The investigation of polycyclic aromatic hydrocarbons (PAHs) is of main importance due to the frequent landfill burning. It consists of an old (non-sanitary) and a new (sanitary) landfill. The old landfill ceased operation in 2021 and was previously ranked among the 50 largest unregulated landfills in the world. The new landfill, with novel leachate treatment, was built according to European Union directives in 2021.

A landfill of this magnitude releases numerous toxic and carcinogenic substances, with PAHs being among the most prevalent (Melnyk et al., 2015). The European Union has identified 16 PAHs (acenaphthene (Ane), acenaphthylene (Ace), anthracene (Ant), benzo(g,h,i)perylene (B[ghi]P), benzo(a)pyrene (B[a]P), benz(a)anthracene (B[a]A), chrysene (Chr), benzo(k)fluoranthene (B[k]F), benzo(b)fluoranthene (B[b]F), dibenz(a,h)anthracene (Db[ah]A), fluorene (Flu), fluoranthene (Fla), indeno(1,2,3-cd)pyrene (In[cd]P), naphthalene (Nap), phenanthrene (Ph), pyrene (Py)) as priority pollutants, due to their mutagenicity and carcinogenicity. These compounds can occur in the environment in high concentrations, are highly persistent, and can travel long distances through the atmosphere (Franco et al., 2017).

Table 1. Description of analysed soil samples.

Sample (S)	Description
S1	old landfill, near leachate
S2	old landfill, near trees
S3	old landfill, near dirt road
S4	old landfill, near dirt road and leachate
S5	old landfill, soil with leachate
S6	old landfill, near waste
S7	top of the old landfill,
S8	new landfill

This experiment was conducted to identify the PAHs and to determine their concentrations in soil samples collected from the *Vinča* landfill. Since the samples were taken from various locations across the landfill, their values can be compared based on the surrounding environmental conditions or by the assessment of PAH origin.

2. Method

Eight soil samples were sieved to a particle size of 630 μm. PAHs were extracted using the Soxhlet method, for 10 h at 200°C. Then they were evaporated and cleaned up using a column filled with silica gel deactivated with 5% water. The purified aromatic fraction was analysed using gas chromatography with mass spectrometry (GC-MS).

3. Results and Discussion

Lower PAHs such as Nap, Ane and Flu were detected in trace concentrations in the analysed soil likely due to their high volatility. Ace (3.09E-05− 9.53E-05 mg/kg) is detected in S5, S6, and S8, with the highest concentration in S6. PAHs detected in all samples are: Fla (7.05E-04− 2.15E-02 mg/kg), with the highest concentration in S4; Py (2.25E-04−1.87E-02 mg/kg), the highest concentration is in S6; B[a]A (9.66E-05− 8.31E-03 mg/kg), with the

highest concentration in S6; Chr (6.61E-04− 1.85E-02 mg/kg), with the highest concentration in S4; B[a]P (2.78E-04− 1.06E-02 mg/kg), the highest concentration was detected in sample S6; B[ghi]P (1.59E-04−8.81E-03 mg/kg), with the highest concentration in S5. Ph (2.34E-04−9.85E-03 mg/kg) is present in all samples except S2, S3, and S5, with the highest concentration in S4. Ant (4.13E-05−2.95E-04 mg/kg) is present only in S6, S7, and S8, with the highest concentration in S8. All samples, except S2 and S3, contain B[b]F (1.28E-03 to 1.16E-02 mg/kg) with the highest concentration present in S6. In S4, S5 and S7 it is found together with B[k]F. In combination with B[k]F, it is present in the range from 4.45E-03 to 2.06E-02 mg/kg, with the highest concentration in S4. B [k]F, in addition to the mentioned samples, is found in all samples with a concentration range of 4.85E-04− 1.86E-02 mg/kg, with the highest concentration in S6. All samples, except S2, contain In[cd]P (range: 2.41E-04 – 1.38E-02 mg/kg), with the highest concentration found in S6. Db[ah]A is present in S4 (2.93E-03 mg/kg) and S7 (8.09E-04 mg/kg). The concentrations of PAHs (medians) in the analysed samples decrease in the following order: B[b]F > Fla > Py > Chr > In[cd]P > B[ghi]P > B[k]F > Ph > Db[ah]A > B[a]P > B[a]A > Ant > Ace. The highest concentrations of PAHs most often came from S6, located near the old part of the landfill near the deposed garbage (Table 1). Also S4, from the old landfill located close to the dirt road and leachate (Table 1). Both samples were collected from an old landfill, once classified as one of the largest in Europe, where frequent occurrences of spontaneous combustion were observed. According to Figure 1, the analysed PAHs mostly originate from petrogenic sources as well as biomass and coal combustion. Although the old landfill is no longer in use and is largely covered with soil, certain areas still contain exposed waste and leachate. Additionally, sporadic self-ignition continues to occur in localized sections of the old landfill, contributing to elevated concentrations of PAHs. In contrast, the lower concentrations of PAHs observed at the new landfill may be attributed to daily soil covering practices and the implementation of leachate management systems.

4. Conclusion

Variations in PAH concentrations among the different samples from the *Vinča* landfill are expected, as these concentrations can be influenced by multiple factors, including the type of waste at a certain location, its environment, the impact of combustion, and the presence of petroleum products. Based on the origin assessment, the results indicate that the predominant sources of the analysed PAHs are of petrogenic origin, as well as biomass and coal combustion. Although the measured concentrations are not higher than those recommended by the National Regulation − 1 mg/kg, they originate from the soil used to cover the old landfill site four years ago, as well as the soil currently used for the daily coverage of the new landfill. Nevertheless, landfills represent a significant source of PAHs, with the potential for their migration into the surrounding environment (water, soil, and air). Therefore, continued monitoring and the implementation of effective landfill management strategies are essential for minimizing associated environmental and human health risks.

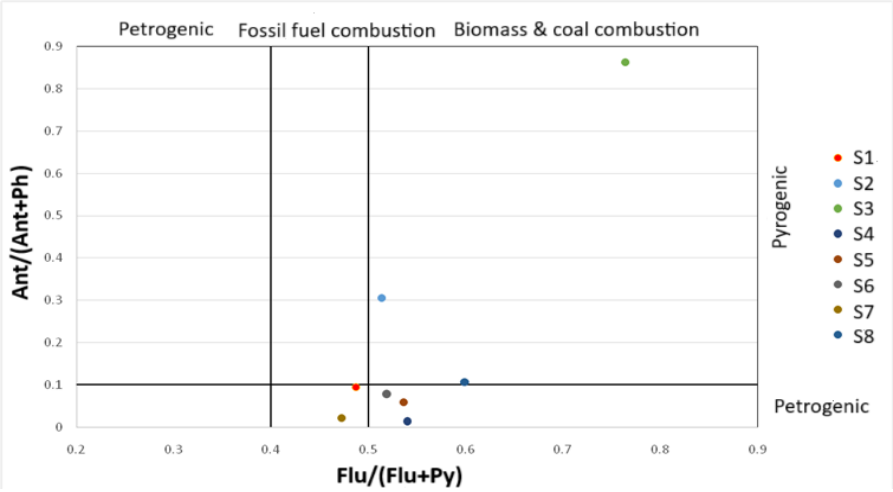

Figure 1. Cross plots presenting the ratios of Ant/(Ant + Ph) vs Flu/(Flu+Py).

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