

LEVELS OF POLYCYCLIC AROMATIC HYDROCARBONS IN MONITORING WELLS FROM MUNICIPAL LANDFILL DETERMINED BY SOLID-PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION

Mirela Miclean¹, Adriana Gog¹, Erika Levei¹, Marius Roman¹, Ioan Stefan Groza²

¹INCDO-INOE 2000, Research Institute for Analytical Instrumentation, 67 Donath, 400293 Cluj-Napoca, Romania, Phone: + 40 264 420590, Fax: + 40 264 42066, e-mail: mirela.miclean@icia.ro

²University of Agricultural Sciences and Veterinary Medicine, Faculty of Veterinary Medicine, 3-5 Manastur St., 400372, Cluj-Napoca, Romania, Phone: + 40 264 596384, Fax: + 40 264 593794, e-mail: isgroza@yahoo.com

ABSTRACT

This study reports the levels of 16 polycyclic aromatic hydrocarbons (PAHs) in the monitoring wells from a municipal landfill. The used analytical method for the simultaneous determination of PAHs was the solid-phase microextraction (SPME)–gas chromatography (GC)–flame ionization detection (FID). Total PAHs concentrations in the samples varied between 1.75 and 9.01 µg/l, with benzo[a]pyrene the most predominant species and reflect the spatial distribution of the monitoring wells.

INTRODUCTION

Landfilling is the most widespread technology for the treatment of urban solid wastes. The main environmental concern regarding the municipal landfill sites is the landfill leachate, a highly contaminated wastewater with a wide range of chemical contaminants (Žgajnar Gotvajn et al., 2009; Wu et al., 2011). Among the numerous contaminants of the leachate, polycyclic aromatic hydrocarbons (PAHs) are of particular interest due to their high persistency and low degradability in the environment and also their powerful toxicity. For instance, some of the PAHs are carcinogens, mutagens, teratogens and induce estrogenic effects (Song et al., 2006; Amorim et al., 2009; EPA, 2011).

This study reports the concentrations of PAHs in five monitoring wells from a municipal landfill, belonging to a city with approximately 140000 inhabitants, situated in the North-Western part of Romania. The samples, collected in triplicate in May 2011 were analyzed using solid-phase microextraction (SPME) technique coupled with capillary gas chromatography with flame ionization detection (GC-FID).

SPME was introduced in 1989 as a solvent-free extraction technique which integrates sampling, clean-up and pre-concentration into a single step. The most widely used format is a silica rod which is coated with a thin film of extraction phase, such as polydimethylsiloxane (PDMS). After extraction has taken place, the loaded SPME fiber is easily introduced into an injection port of a GC instrument for thermal desorption (Hutchinson et al., 2007).

MATERIALS and METHODS

Reagents and materials

The mixture standard solution (DE-PROM 16) containing 16 compounds, each at 100 µg/ml was obtained from LGC Standards (Germany). The analytes were: acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, chrysene, benzo[b]-fluoranthene, benzo[k]-fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[ghi]-perylene, fluoranthene, fluorene, naphthalene, phenanthrene, pyrene. Toluene and sodium chloride were of analytical grade and provided by Merck (Darmstadt, Germany).

The SPME holder and fiber assemblies for manual sampling were provided by Supelco. The fiber coatings assayed was poly(dimethylsiloxane) (PDMS, 100 µm).

SPME extraction

Fibres were conditioned in the injection port of a gas chromatograph for 1 h according to the manufacturer's instructions before use. Blank desorptions of the fibre were carried out to ensure no contamination was present both before and during use.

SPME extractions were performed by direct immersion of fiber in 20 mL water sample, into 20 mL vial capped with PTFE-coated septa. The analytes were extracted for 45 min at 25°C with 25 w/v% NaCl, according to the method described by King et al., (2004). After the extraction, the fiber was thermally desorbed for 5 min into the glass liner of the gas chromatograph injector at 290°C.

GC-FID analysis

Analysis was performed by exposing the fibre to an Agilent Technologies GC-FID (6890) with an HP-5 (5% phenyl:95% dimethylpolysiloxane, 30 m x 0.25 mm, 0.25 µm film thickness) fused-silica capillary column. The injector port temperature and the detector were set to 290°C and 300°C, respectively. The GC temperature was programmed as follows: from 50 (2 min) to 300°C at a rate of 6°C/min where it was held for 5 min. The target compounds were quantified by external calibration using mix standard solution diluted in toluene.

RESULTS

In all the investigated samples, the concentrations of acenaphthylene, chrysene, benzo[b]-fluoranthene, benzo[k]-fluoranthene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, benzo[ghi]-perylene, fluorene, naphthalene, phenanthrene were below the detection limits.

The limits of detection, determined using the 3σ criteria varied in the range 2 ng/l (for fluoranthene and pyrene) to 36 ng/l (for benz[a]anthracene).

Total PAH concentrations in the samples are shown in Table 1 and varied between 1.75 and 9.01 µg/l, with benzo[a]pyrene the most predominant species.

Table 1. Total PAH concentrations in the monitoring wells

Sample	Total PAH concentration, µg/l
Sample 1	4.12
Sample 2	3.12
Sample 3	1.75
Sample 4	7.00
Sample 5	9.01

The concentrations of PAHs in the 5 monitoring wells are graphically shown in Figure 1.

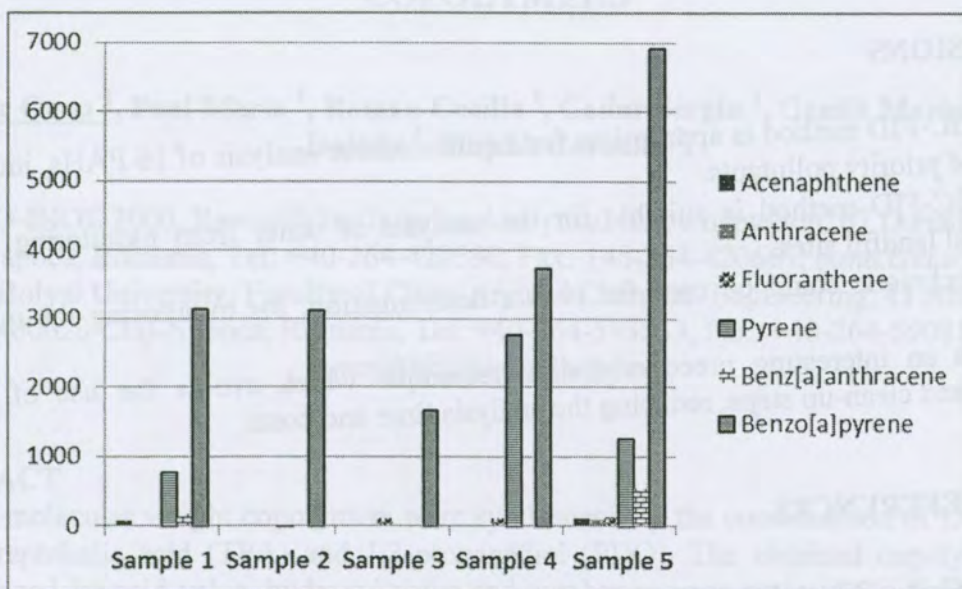


Figure 1. Concentrations of PAHs in the monitoring wells (ng/l)

The chromatogram obtained for sample 5, for example, is shown in Figure 2, emphasizing the obtained compounds: acenaphthene, anthracene, fluoranthene, pyrene, benz[a]anthracene and benzo[a]pyrene.

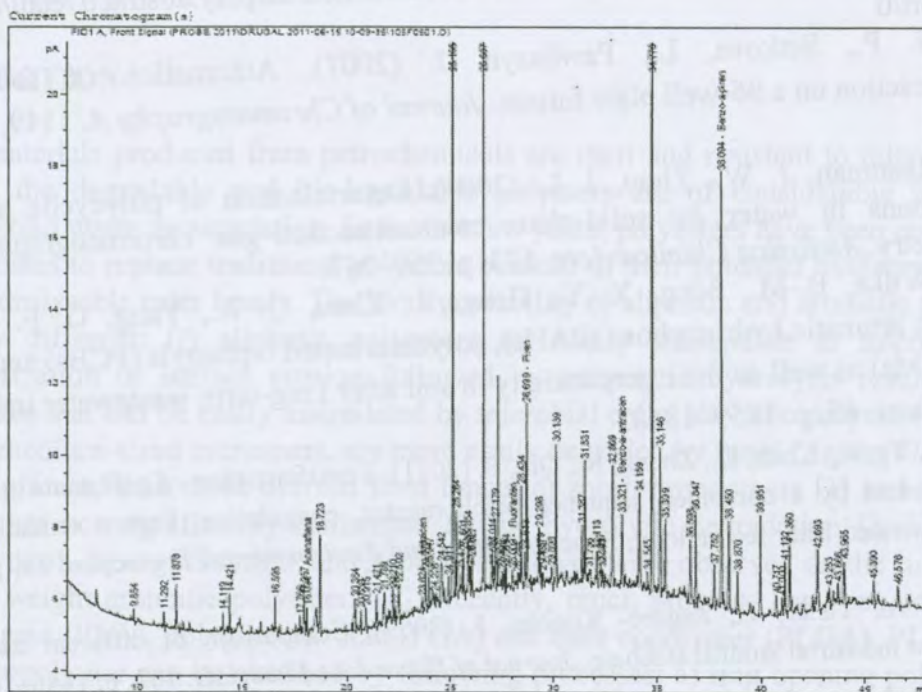


Figure 2. The GC-FID chromatogram of the sample 5

The obtained concentrations reflect the spatial distribution of the monitoring wells related to the underground water flow. In the wells situated upstream and in the side of municipal landfill, the PAHs levels are low (samples 1, 2 and 3) due to the fact that underground water collects waters from uncontaminated area. In the wells located downstream of landfill, the

concentrations are higher (samples 4 and 5), taking into consideration that underground water collects the landfill leachates.

CONCLUSIONS

- SPME-GC-FID method is appropriate for a multi-residue analysis of 16 PAHs, included in the list of priority pollutants.
- SPME-GC-FID method is suitable for the analysis of water from monitoring wells in municipal landfill sites.
- SPME technique could be used for *in situ* determination, for monitoring the quality of water.
- SPME is an interesting preconcentration technique which avoids the use of organic solvents and clean-up steps, reducing the analysis time and costs.

LIST OF REFERENCES

- Amorim, L. C. A., Dimandja, J.-M., de Lourdes Cardeal, Z. (2009). Analysis of hydroxylated polycyclic aromatic hydrocarbons in urine using comprehensive two-dimensional gas chromatography with a flame ionization detector, *Journal of Chromatography A*. 1216, p. 2900–2904.
- EPA, 2011, available at:
http://cfpub.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/173/report/0
- Hutchinson, J. P., Setkova, L., Pawliszyn, J. (2007). Automation of solid-phase microextraction on a 96-well plate format. *Journal of Chromatography A*. 1149, p. 127–137.
- King, A. J., Readman, J. W., Zhou, J. L. (2004). Determination of polycyclic aromatic hydrocarbons in water by solid-phase microextraction–gas chromatography–mass spectrometry. *Analytica Chimica Acta*. 523, p. 259–267.
- Song, Y. F., Wilke, B.-M., Song, X. Y., Gong, P., Zhou, Q. X., Yang, G. F. (2006). Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals (HMs) as well as their genotoxicity in soil after long-term wastewater irrigation. *Chemosphere*. 65, p. 1859–1868.
- Wu, Y., Zhou, S., Ye, X., Chen, D., Zheng, K., Qin, F. (2011). Transformation of pollutants in landfill leachate treated by a combined sequence batch reactor, coagulation, Fenton oxidation and biological aerated filter technology. *Process Safety and Environmental Protection*. 89, p. 112–120.
- Žgajnar Gotvajn, A., Tisler, T., Zagorc-Končan, J. (2009). Comparison of different treatment strategies for industrial landfill leachate. *Journal of Hazardous Materials*. 162, p. 1446–1456.