

Assessment of soil contamination by oil-derived compounds in the Kielce agglomeration using gas chromatography coupled with mass spectrometry (GC-MS)

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Abstract. Soil contamination with petroleum-derived compounds is one of the most serious ecological problems. Their main source in urbanized areas is public transport. According to the Regulation of the Polish Minister of Environment about the assessment of earth's surface contamination, hydrocarbon compounds are divided into: gasolines and oils, aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). The subject of the research is the use of a gas chromatography coupled with mass spectrometry (GC-MS) method to assess the degree of soil contamination in the vicinity of the main communication routes of the Kielce agglomeration. This method is useful for the detection and identification of many organic compounds occurring in samples in very small quantities, which cannot be determined by common methods. For the purpose of this study, 14 soil samples were collected. After carrying out extraction with various methods, the ultrasonic solvent extraction method was chosen as the most effective way of extracting hydrocarbon impurities for the GC-MS studies. During single analysis, both oil fraction and PAHs quantities were determined.

1 Introduction

A municipality can be compared to a living organism, where all elements should function harmoniously. Soil in urban agglomerations plays the role of a connective tissue, which binds together and supports other elements of the urban organism, whereas streets can be compared to a circulatory system. Each living organism, as a result of its life activity, produces metabolites that can accumulate in its tissues. One of the groups of urban metabolites are organic pollutants, especially petroleum-derived compounds and polycyclic aromatic hydrocarbons (PAHs).

The main source of oil-related pollution is petrochemical and transport industry. PAHs, a group of persistent organic pollutants with two or more connected aromatic rings, has more sources in the environment [1-3].

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PAHs can be generated in natural combustion processes (meadows and forests fires) or may have an anthropogenic origin. In the latter case the origin may be petrogenic, i.e. related to oil and its products (e.g. catalytic cracking of oil or abrasion of vehicle tires) and coal (coke production), as well as pyrogenic origin, i.e. connected with all processes of fuel combustion in the production of electricity and heat and in internal combustion engines [1-3].

Every release of hydrocarbons into the environment causes a significant interference during which mainly soil and water environments receive this group of compounds. Petroleum-derived compounds in soil inhibit gas exchange, reduce oxygen content in soil air and in soil water, disturb the homeostasis of soil environment and, as a consequence, restrain the growth or even cause the death of edaphon and flora in the contaminated area. Moreover, the petroleum-derived compounds, especially PAHs, exhibit toxic, carcinogenic and mutagenic effects. PAHs increase the risk of skin and systemic cancers such as lung, bladder and stomach cancer. [4-10]. Therefore, ongoing research is being carried out, existing methods of analysis and assessment of environmental pollution are being improved and new methods are sought.

This study is an attempt at showing the applicability of the gas chromatography method coupled with mass spectrometry (GC-MS) - a quick and effective analytical methodology for assessing the degree of soil contamination. The measurements were performed on the Kielce agglomeration soil samples. The described method allows quick and effective identification of PAHs, i.e.. naphthalene (NPH), phenanthrene (PHE), anthracene (ATH), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHRY), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(e)pyrene (BeP), dibenzo(a,h)anthracene (DBahA), benzo(a)pyrene (BaP), indeno(1,2,3-c,d)pyrene (IcdP), benzo(ghi)perylene (BghiPE) and evaluation the hydrocarbon content of oil fraction (sum of C₁₂ – C₃₅ hydrocarbons) in soils during single analysis.

2 Samples and method

The research was carried out on soil samples taken from a depth interval of 0.15 m to 0.25 m at a distance of 3 m and 13 m from 6 selected streets of the Kielce agglomeration: Krakowska St. (K-3, K-13, KT-3, KT-13), Tarnowska St. (T-3, T-13), Sandomierska St. (S-3, S-13), Radomska St. (R-3, R-13), Warszawska St. (W-3, W-13), and Łódzka St. (L-3, L-13) (Fig. 1). All samples were collected from the vicinity of the largest traffic access roads.

Analytical procedure was based on the US EPA methods no. 8270C and 3550C [11-12]. Homogenized, air-dried soil samples (50 g) were subjected to extraction with hexane at room temperature in an ultrasonic bathtub. To remove residual solid particles, the extracts were filtered through a sintered glass Buchner funnel with porosity grade G3. The solutions were concentrated to a volume of 0.5 cm³, then the 0.5 cm³ of mixture of hexane and standard (1,1'-binaphthyl) was added to each of the samples. The separation of PAHs was carried out using an Agilent Technologies 7890A gas chromatograph coupled with an Agilent 5975C Network mass spectrometer, equipped with a capillary column J&W 123-5562DB-5ms (diameter – 320 μm, film thickness – 0.25 μm, length – 60 m). The carrier gas was helium with a constant flow of 2 cm³/min. The column was thermostated: 80°C for 1 minute, temperature increase 20°C/min to 120°C, then increase of 2°C/min to 180°C and increase of 3°C/min to 300°C (maintaining this temperature for 35 min). The total analysis time was 99 minutes.

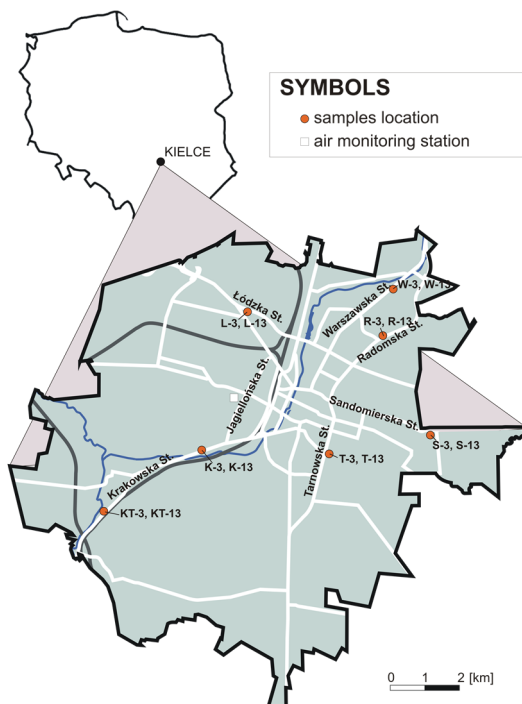


Fig. 1. Samples location.

3 Results and discussion

The results of analyses were presented in the form of chromatograms and tables with the content of PAHs and oil fraction (Table. 1, 2, 3 and Fig. 2).

Table 1. Concentration of LMW (2- and 3- rings) PAHs in soil samples.

Samples	Concentration (mg/kg of soil)			
	2-rings	3-rings		
	NPH	PHE	ATH	FLA
K-3	0.01	0.05	0.01	0.16
K-13	l.i.*	0.09	0.01	0.30
KT-3	0.01	0.09	0.02	0.47
KT-13	l.i.	0.03	0.005	0.16
L-3	0.01	0.04	0.005	0.10
L-13	0.01	0.04	0.01	0.19
R-3	l.i.	l.i.	l.i.	l.i.
R-13	l.i.	l.i.	l.i.	0.01
S-3	l.i.	0.05	0.01	0.24
S-13	l.i.	0.01	l.i.	0.03
T-3	0.01	0.20	0.03	0.62
T-13	0.01	0.60	0.11	1.15
W-3	0.01	0.11	0.02	0.60
W-13	l.i.	0.02	l.i.	0.09
Threshold value	20	-**	20	-

*low intensity, **lack of threshold

Table 2. Concentration of HMW (4-, 5- and 6- rings) PAHs in soil samples.

Samples	Concentration (mg/kg of soil)									
	4-rings			5-rings					6-rings	
	PYR	BaA	CHRY	BbF	BkF	BeP	DBahA	BaP	IcdP	BghiPE
K-3	0.15	0.10	0.12	0.25	0.03	0.13	0.01	0.13	0.14	0.17
K-13	0.26	0.15	0.14	0.24	0.03	0.13	0.01	0.15	0.11	0.13
KT-3	0.44	0.28	0.35	0.73	0.11	0.40	0.03	0.44	0.48	0.59
KT-13	0.15	0.10	0.13	0.24	0.03	0.13	0.01	0.13	0.10	0.11
L-3	0.09	0.04	0.05	0.08	0.01	0.05	0.01	0.05	0.03	0.04
L-13	0.19	0.11	0.13	0.23	0.03	0.24	li.*	0.04	0.06	0.07
R-3	li.	li.	li.	li.	li.	li.	li.	li.	li.	li.
R-13	0.01	li.	li.	li.	li.	li.	li.	li.	li.	li.
S-3	0.27	0.15	0.17	0.31	0.06	0.16	0.02	0.22	0.16	0.17
S-13	0.03	0.01	0.02	0.03	0.01	0.02	li.	0.01	0.01	0.02
T-3	0.52	0.31	0.34	0.55	0.08	0.31	0.02	0.36	0.25	0.29
T-13	0.95	0.52	0.57	0.79	0.10	0.42	0.03	0.56	0.37	0.39
W-3	0.57	0.36	0.41	0.77	0.12	0.44	0.04	0.53	0.46	0.55
W-13	0.08	0.04	0.05	0.10	0.01	0.06	0.01	0.07	0.05	0.06
Threshold value	-**	20	20	20	-	-	20	20	20	20

*low intensity, **lack of threshold

The presence of LMW (Low Molecular Weight which means a sum of 2- and 3-rings) PAHs, as well as HMW (High Molecular Weight which means a sum of 4-, 5- and 6-rings) PAHs was observed in all tested samples (Tabs.1, 2 and Fig. 3), except for samples R-3 and R-13 taken beside Radomska St. They were characterized by PAHs contents below the detection limit, which was probably related to the ground replacement during the expansion of the road in 2007. Low values of PAH's concentrations in this place indicated a low level of environmental pressure exerted by traffic. Among the tested samples, the highest values were obtained in samples collected at Tarnowska St. In all cases, PAHs contents did not exceed the permissible values specified in the Regulation of the Polish Minister of the Environment [13]. Maximal total lifetime cancer risk (TLCR) determined for the entire sample population of $4 \cdot 10^{-5}$ varied between 10^{-4} do 10^{-6} which is an acceptable level of cancer risk. This means that the probability of an individual to develop cancer over the lifetime was 4 in 100 000 [14]. Concentrations of the oil fraction also did not exceed the permissible values specified in the Regulation of the Polish Minister of the Environment [13].

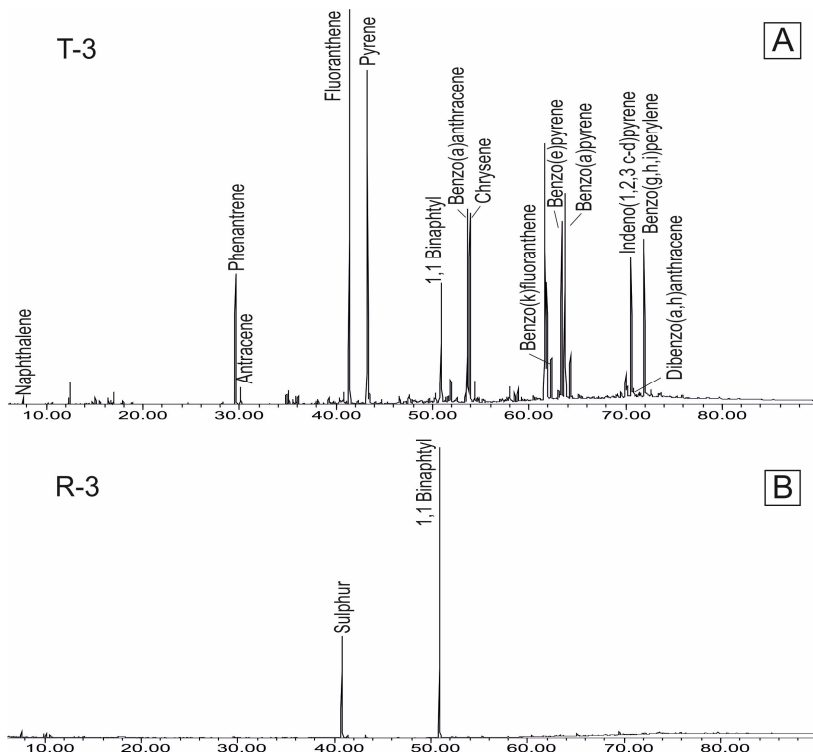


Fig. 2. Distribution of PAHs: (A) contaminated sample, (B) not contaminated sample

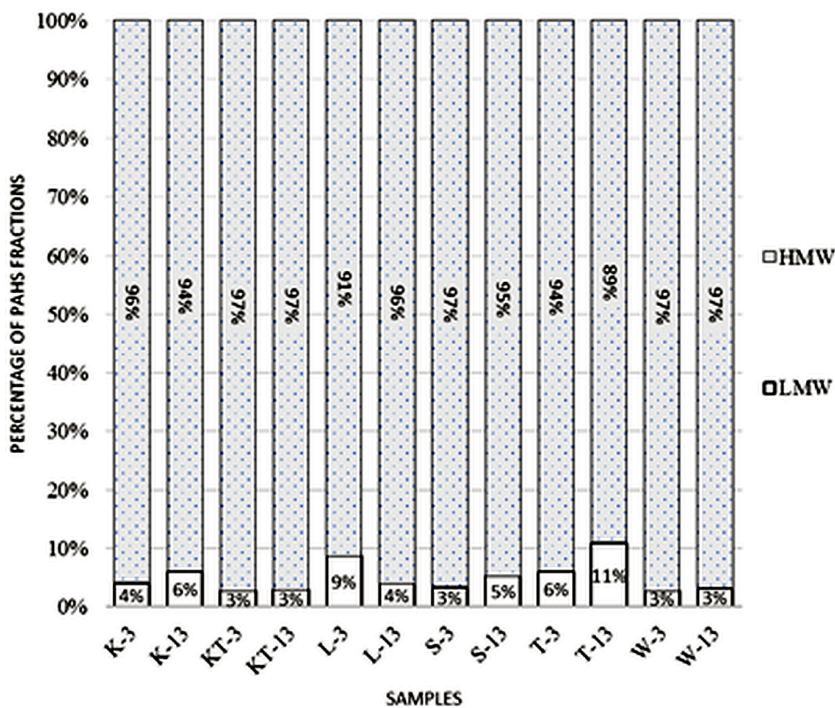


Fig. 3. Percentage of PAHs fractions in analysed soil samples

Table 3. Concentrations of oil fraction and PAHs sum in soil samples

Samples	Oil fraction (mg/kg of soil)	Oil fraction threshold value (mg/kg of soil)	ΣPAHs (mg/kg of soil)
K-3	5.30	3000	1.29
K-13	4.47		1.63
KT-3	9.42		3.88
KT-13	4.13		1.17
L-3	n.a.*		0.54
L-13	n.a.		1.15
R-3	0.99		l.i.**
R-13	1.43		0.02
S-3	4.62		1.75
S-13	1.28		0.18
T-3	8.31		3.53
T-13	13.81		6.11
W-3	11.02		4.39
W-13	1.78		0.55

*not analysed, **low intensity

In many cities, the HMW PAHs account for most of the total PAHs in urban soils [15]. These values are similar as in the Kielce agglomeration. The domination of HMW PAHs shows to the presence of processes during which fuels undergo high-temperature combustion [16]. In all tested samples HMW PAHs are dominated by: fluoranthene, benzo(b)fluoranthene, benzo(ghi)perylene and benzo(a)pyrene.

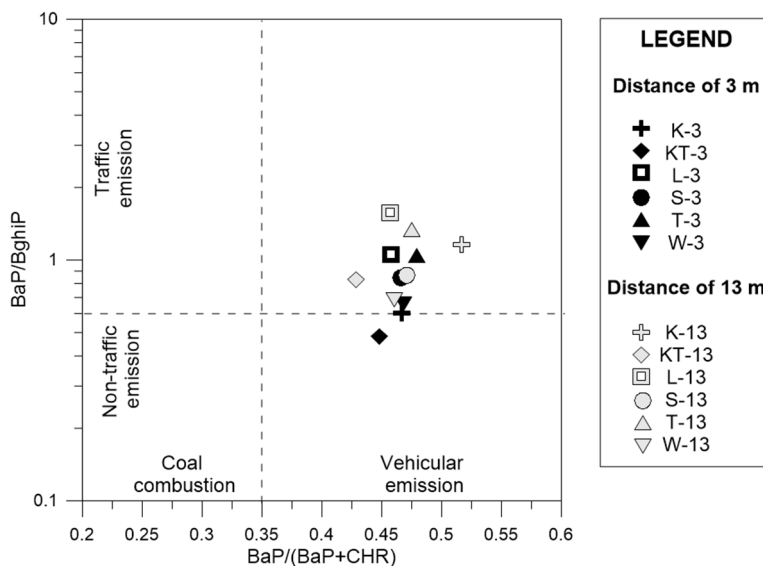


Fig. 4. Cross plot of BaP/BghiP and BaP/(BaP+CHR) ratios (values range after [17,19])

The BaP/(BaP+CHR) and BaP/BghiP ratios show traffic emission from engines [17,19] (Fig. 4). A linear correlation was also observed between the sum of PAHs and the concentration of oil fraction in soil (Fig. 5). This shows that the combustion of fuels in vehicle engines is the main source of PAHs. There was no significant difference between hydrocarbon concentrations at a distance of 3 m and 13 m from the edge of the road, which may indicate that a greater range of contamination comes from communication routes.

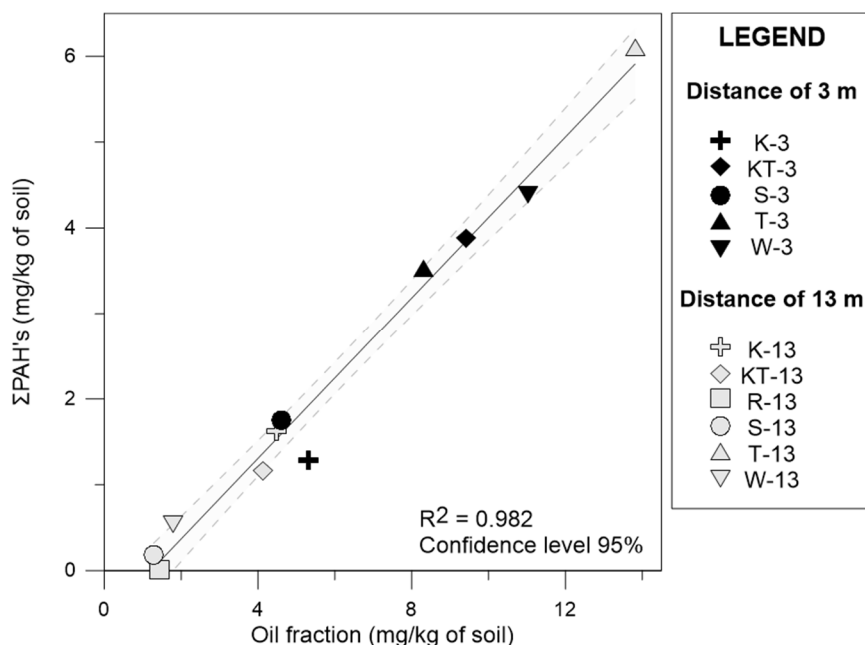


Fig. 5. Correlation of sum of PAHs and concentration of oil fraction in soil

The elements of the environment are closely interconnected. The condition of the pedosphere could be used as a general, long-term indicator of the state of urban environment. It could be illustrated by a comparison of the results of soil analyses with annual average concentrations of PM10 and PAH's in PM10 obtained from the main air - quality monitoring station localised in the city centre in Jagiellońska St. (Table. 4, Fig. 6) provided by the Polish Chief Inspectorate of Environmental Protection. The annual average threshold for PM10 concentration in the air is 50 ppm. For the last 7 years this value has not been exceeded. Moreover, the concentration of PM10 has gradually decreased year after year. The concentrations of selected PAHs generally stayed constant, but with the decreasing amount of given matter in air the absolute amount of PAHs introduced into the soil.

Table. 4. Concentration of PM10 and selected PAH's monitored in station at Jagiellońska St.

Years	Selected PAH's concentration in PM10 [ppm]					PM10 [ppm]
	BaP	BbF	BkF	DBahA	IghiP	
2010	3.36	3.10	1.66	0.59	1.81	41.9
2011	7.01	6.25	2.79	0.80	3.67	43.5
2012	7.92	7.63	3.42	1.13	5.66	41.0
2013	4.52	5.80	2.42	0.73	5.34	38.1
2014	3.83	4.78	1.91	1.08	3.00	37.3
2015	5.42	8.26	2.66	1.33	3.95	36.8
2016	4.38	5.77	2.24	1.18	3.35	32.8
2017	5.88	5.02	2.65	1.77	3.97	35.2

Lack of thresholds exceed in air could be compare with similar observations in quality of soil. Furthermore, the increasing quality of air is reflected in soil samples R-3 and R-13 in which ground was replaced and present concentration of analysed pollutants is under detection threshold. Replacement could case move uncontained part of soil to surface, so lack of contamination in that location indicate rather good conditions of environment. Good quality of air, confirm, that the contamination in polluted samples is strong connected with traffic.

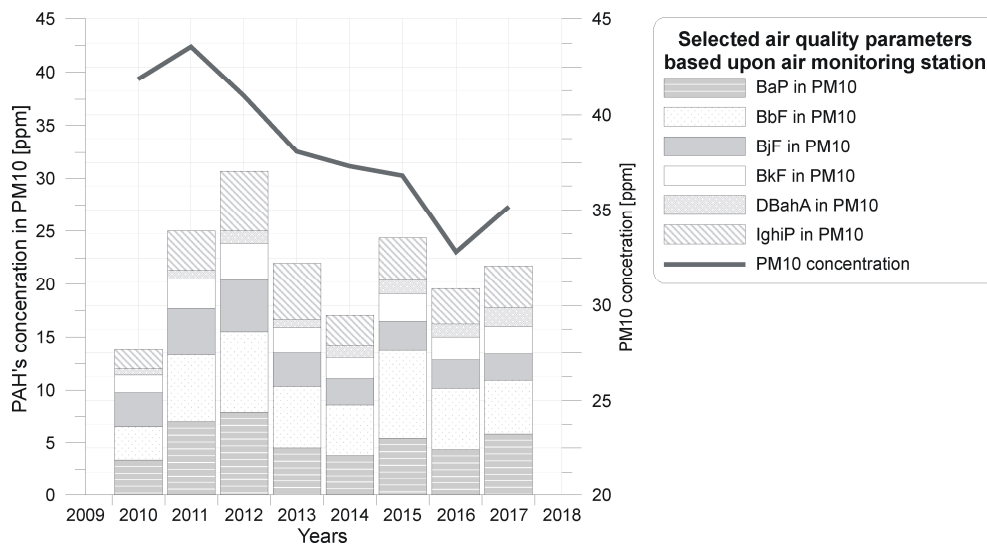


Fig. 6. Concentration of PM10 and selected PAH's monitored in station at Jagiellońska St.

4 Conclusions

- In all tested soil samples, PAHs content and concentration of oil fraction do not exceed the permissible values specified in the Regulation of the Minister of the Environment.
- Kielce agglomeration is characterized by the domination of HMW PAHs, which indicates that processes lying in high temperature combustion of fuels were involved.
- The BaP/(BaP+CHR) and BaP/BghiP ratios show traffic emission from engines.
- A linear correlation between the sum of PAHs and concentration of oil fraction in soil indicates that the main source of PAHs is combustion of oil in vehicle engines.
- Sticking to the threshold values for air could be compared to similar qualitative observations for soil. There were no significant differences between hydrocarbon concentrations at a distance 3 m and 13 m.

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