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Soil Contamination with Polycyclic Aromatic Hydrocarbons in the Vicinity of the Ring Road in Siedlce City

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Abstract

The aim of this work was to establish a level of polycyclic aromatic hydrocarbons (PAHs, recognised by the World Health Organisation as mutagenic and carcinogenic compounds) in samples of soil collected along the ring road in city Siedlce, which is an element of the main route Berlin-Moscow. Our investigation was carried out in selected points of collecting the samples since April to October 2000, i.e. in a period of growth and final vegetation of plants. Analysis was carried out using Solid Phase Extraction (SPE) and reverse phase High Performance Liquid Chromatography (HPLC). Concentrations of individual compounds were between 10^{-7} and 10^{-9}mg kg^{-1}.

Keywords: analysis, HPLC, polycyclic aromatic hydrocarbons (PAHs), SPE

Introduction

Contamination is an unavoidable effect of development in technology and transport. As a result of industrialisation and intensity of traffic there appears to be a real danger for ecosystems and human health. Among pollutants produced by transport and industry, polycyclic aromatic hydrocarbons (PAHs) deserve particular attention due to carcinogenic and mutagenic activity. In a period of intensive increase of tumour diseases an estimation of the level of PAHs seems to be important.

Characteristic for PAHs is their relatively quick degradation. Medium half-life period of these compounds in the environment is about one month.

The main reason of investigations in this area is strong carcinogenic and mutagenic activity of PAHs. Generally, the most injurious for human organisms are compounds containing 4-6 condensed benzene rings in a molecule. The common distinctive mark of PAHs is their restricted local effect and long period between first contact with a compound before appearance of a tumour. They are dangerous even in trace amounts; therefore, controlling the PAH level seems to be a substantial contemporary ecoanalytical problem.

In nature PAHs exist in different structural forms and in a wide range of molecular mass. Because of high molecular weight and lack of polar groups they are slightly soluble in water (benzo[a]pyrene 4 μg/dm^3, fluorene 265 μg/dm^3). Therefore, the majority of PAHs are suspensions [1-3]. However, the presence of detergents and other organic compounds improves solubility. The problem of PAH solubility in water and their carcinogenic activity has been investigated by many authors [4-6].

Up to the beginning of the last century there existed a balance between production of PAHs and their microbiological or photochemical degradation. Rapid development of industry and intensive progress of transport caused immense requirements for fuel. As a consequence of errors or accidents during storage, conversion and distribution of fuel for these products often penetrates the environment and causes real danger. Accidents of contamination of environment with fuel, oils and lubricants can be estimated as 40% of all cases of soil pollution [5]. After penetration of hydrocarbons to the environment their concentration and structure is changing. They are subjected to abiotic processes (evaporation, washing out, photolysis and reduction) and, what is more important, to biological processes, i.e. absorption by plants and soil fauna.

Soil, because of sorption properties, accumulates an immense amount of pollutants, including PAHs. Most of these compounds are transported by air with particles of dust. PAHs can be adsorbed by the soil, but also by leaves and roots of plants. Biodegradation of PAHs in plant tissues is a relatively slow process and after decaying of plants they remain in the soil [6]. Therefore, the level of PAHs in soil is a result of the amount of compounds coming with dust, sewage or compost and the amount of compounds removed by evaporation, washing, biodegradation or chemical decomposition [7,8]. Degradation can be carried out by solar radiation and as a result more toxic products [9]. Microorganisms cause numerous transformations of PAHs. The rate of these processes depends on many factors (access of microorganisms to pollutants, contents of other organic substances necessary for microorganisms, the presence of water) [10]. Limited solubility in water and as a consequence a strong tendency to absorption in mould layer of soil make for difficult utilisation of PAHs by microorganisms [11]. Access to water makes possible transport of microorganisms, removing metabolites from their cells. On the other hand, it makes diffusion of substrates and nutrition to the cells. It results in a decrease of aromatic ring number facilitates biodegradation of PAHs. Many products of PAH biodegradation are more harmful than the parent compounds [12].

Absorption of PAHs by plants from soil can carry into the presence of these compounds in the human alimentary chain. Because of slight solubility in water and strong sorption affinity to soil, coefficients of transfer soil-plant are relatively low. Nevertheless, plants can be contaminated by PAH as a result of sorption on roots or tubers or settling on leaves and fruits together with dust. Human exposure to PAHs is 88-98% connected with food (in 5% with food of plant origin) [9-13]. PAH can penetrate food indirectly – from air or water and directly, e.g. during smoking. Permissible amounts of PAH in smoked product, in western countries is 1 µg/kg. Content of PAH in fruits and vegetables depend on pollution of environment (mainly on air pollution) and on area of contact. For example, apples contain usually 0.2-0.5 µg/kg [12], tomatoes 0.2 µg/kg, spinach 6.6 µg/kg, cabbage (savoy) 20.4 µg/kg. The majority of hydrocarbons are situated on the skin of fruits and vegetables [11-13].

Therefore, the problem of purity of soil is of great importance. However, information dealing with actual levels of PAHs in soil is insufficient because of numerous analytical difficulties connected with determination of PAH and unsatisfied number of approved procedures. Regulations concerning content of these compounds in soil in Poland are in preparation. The most known and often used are regulations worked out in Holland (so-called Dutch list: list of PAHs and classification of soils according to content of PAH) [14-17].

Materials and Methods

This study was conducted along the ring road surrounding the city of Siedlce. The road passes through fields and as a sector of the main route Berlin-Moscow sees intensive traffic (Fig.1). The samples of soil were collected from a depth of 0-20 cm and 15 m distance from the shoulder of the road and not less than 150-200 m from buildings.

The sample was dried at room temperature to constant weight, then (15 g) extracted in a Soxhlet apparatus for 8 hours with hexane (150 cm^3). The extract was concentrated by evaporation. The residue (2-5 cm^3) was subjected to solid phase extraction (SPE) on a column (3 cm^3) packed with chemically modified silica [12]. SPE column was washed earlier with hexane (3 x 4 cm^3). PAHs were eluted by a mixture of toluene and acetonitrile (1:3); (3 x 3 cm^3). The eluate was evaporated, the residue dissolved in 2 cm^3 of acetonitrile and chromatographed.

Fig.1. The location of the sampling stations (**P**) in the road in Siedlce.

Table 1. Content of PAHs in soil samples (mg·kg^{-1}) measuring point P-1.

Compound	May	July	September
Naphthalene	2.9 x 10^{-7} ± 0.04	1.2 x 10^{-6} ± 0.02	9.1 x 10^{-7} ± 0.46
Acenaphthylene	2.3 x 10^{-7} ± 0.03	2.3 x 10^{-8} ± 0.08	7.6 x 10^{-7} ± 0.38
Acenaphtene	2.1 x 10^{-7} ± 0.03	1.1 x 10^{-7} ± 0.05	nd
Fluorene	2.2 x 10^{-7} ± 0.04	1.2 x 10^{-7} ± 0.05	1.1 x 10^{-8} ± 0.06
Phenanthrene	3.4 x 10^{-8} ± 0.11	2.3 x 10^{-8} ± 0.12	3.0 x 10^{-8} ± 0.15
Anthracene	4.7 x 10^{-8} ± 0.18	3.7 x 10^{-9} ± 0.16	1.4 x 10^{-8} ± 0.07
Fluoranthene	2.7 x 10^{-8} ± 0.09	nd	nd
Pyrene	1.3 x 10^{-8} ± 0.05	8.5 x 10^{-8} ± 0.40	1.6 x 10^{-8} ± 0.08
Benzo(a)anthracene	1.4 x 10^{-8} ± 0.06	3.9 x 10^{-8} ± 0.16	6.9 x 10^{-8} ± 0.32
Chrysene	nd	nd	nd
Benzo(b)fluoranthene	1.1 x 10^{-9} ± 0.05	2.3 x 10^{-8} ± 0.12	3.1 x 10^{-9} ± 0.15
Benzo(k)fluoranthene	3.1 x 10^{-7} ± 0.13	1.9 x 10^{-8} ± 0.07	3.0 x 10^{-8} ± 0.13
Benzo(a)pyrene	nd	nd	nd
Dibenzo(a,h)anthracene	2.4 x 10^{-7} ± 0.12	3.2 x 10^{-8} ± 0.11	1.1 x 10^{-7} ± 0.03
Benzo(g,h,i)perylene	nd	nd	3.1 x 10^{-8} ± 0.12
Indeno[1,2,3-c,d]pyrene	nd	nd	nd

nd - not detected

HPLC analysis was performed using Shimadzu instrument equipped with Rheodyne Model 7125 injector with 20µl sample loop, a column (250 x 4 mm) packed with Si 60-ODS (particle size 10 µm), UV detector SPD-6 and integrator C-R6A. The mobile phase consisted of aqueous methanol (70%, v/v). Flow rate was 1 cm^3 min^{-1}.

Results and Discussion

Medium contents of determinated hydrocarbons in investigated samples of soil are situated between 10^{-6} (for naphthalene, Table 2) and 10^{-9} mg·kg^{-1} (for benzo[k]fluoranthene, Table 3). Slightly higher contents of some hydrocarbons in May compared to September (e.g. naphthalene – Tables 2 and 3, benzo[k]fluoranthene – Table 1, 2 and 3, anthracene – Table 1) indicate that in winter PAHs derived from combustion gas, grease, petrol products and atmospheric contaminants (dust, smoke) are cumulated on the soil surface and after melting of snow penetrate the mould layer of soil (Fig.2). In May 2000 weather conditions, which mainly determines content of PAHs in air, were not favorable for self-purification (median sum of rainfall 24.6 mm·m^{-2}, median temperature 16.4°C [18,19]. Therefore, contents of major part of investigated hydrocarbons are higher than in May (e.g. 3.1 x 10^{-8} for phenanthrene, 8 x 10^{-8} for benzo[a]pyrene – Table 2 and 7.6 x 10^{-7} for acenaphthylene, 6.9 x 10^{-8} for benzo[a]anthracene – Table 1. This dependence can be explained by relative high amounts of rainfall in summer (medium rainfall in July 155.9 mm·m^{-2}, medium temperature 19.0°C). PAH concentration in soil could in September be even higher, but good conditions occurred for development of microflora, which is active towards

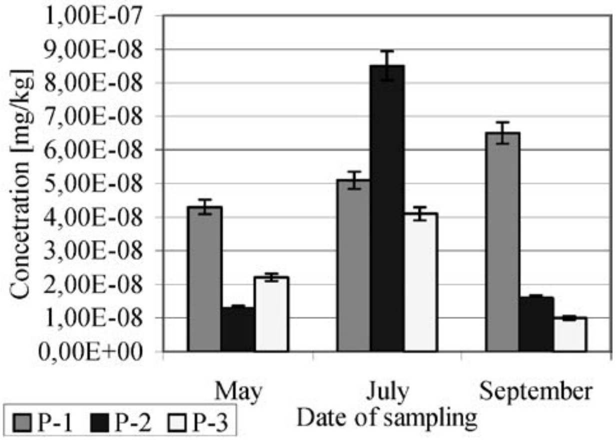

Fig.2. Changes of pyrene concentration [mg/kg] in soil in the vicinity of ring road in Siedlce city in year 2000.

Table 2. Content of PAHs in soil samples (mg·kg^{-1}) measuring point P-2.

Compound	May	July	September
Naphthalene	1.1 x 10^{-6} ± 0.05	3.4 x 10^{-7} ± 0.04	5.1 x 10^{-7} ± 0.21
Acenaphthylene	3.0 x 10^{-7} ± 0.04	1.0 x 10^{-7} ± 0.03	nd
Acenaphtene	1.0 x 10^{-7} ± 0.01	3.3 x 10^{-8} ± 0.04	1.4 x 10^{-7} ± 0.08
Fluorene	1.4 x 10^{-7} ± 0.02	1.1 x 10^{-7} ± 0.04	1.3 x 10^{-7} ± 0.06
Phenanthrene	1.1 x 10^{-8} ± 0.02	1.5 x 10^{-8} ± 0.01	3.1 x 10^{-8} ± 0.09
Anthracene	1.0 x 10^{-8} ± 0.01	2.7 x 10^{-8} ± 0.02	3.4 x 10^{-8} ± 0.11
Fluoranthene	1.1 x 10^{-8} ± 0.01	2.1 x 10^{-8} ± 0.03	5.0 x 10^{-8} ± 0.20
Pyrene	2.2 x 10^{-8} ± 0.02	4.1 x 10^{-8} ± 0.02	1.0 x 10^{-8} ± 0.02
Benzo(a)anthracene	nd	3.0 x 10^{-8} ± 0.11	4.0 x 10^{-8} ± 0.11
Chrysene	1.1 x 10^{-8} ± 0.01	nd	nd
Benzo(b)fluoranthene	2.3 x 10^{-9} ± 0.12	1.4 x 10^{-8} ± 0.02	2.7 x 10^{-9} ± 0.03
Benzo(k)fluoranthene	2.3 x 10^{-7} ± 0.03	2.4 x 10^{-7} ± 0.03	7.6 x 10^{-8} ± 0.09
Benzo(a)pyrene	7.1 x 10^{-7} ± 0.14	6.0 x 10^{-7} ± 0.21	8.0 x 10^{-8} ± 0.25
Dibenzo(a,h)anthracene	8.1 x 10^{-8} ± 0.31	3.3 x 10^{-8} ± 0.12	1.2 x 10^{-8} ± 0.03
Benzo(g,h,i)perylene	nd	nd	3.3 x 10^{-8} ± 0.12
Indeno[1,2,3-c,d]pyrene	nd	nd	nd

nd - not detected

Table 3. Content of PAHs in soil samples (mg·kg^{-1}) measuring point P-3.

Compound	May	July	September
Naphthalene	1.3 x 10^{-7} ± 0.02	1.1 x 10^{-6} ± 0.01	1.8 x 10^{-8} ± 0.02
Acenaphthylene	2.3 x 10^{-8} ± 0.04	2.5 x 10^{-8} ± 0.04	4.2 x 10^{-8} ± 0.14
Acenaphtene	nd	4.9 x 10^{-8} ± 0.04	4.8 x 10^{-8} ± 0.14
Fluorene	1.6 x 10^{-8} ± 0.04	2.3 x 10^{-8} ± 0.04	5.6 x 10^{-7} ± 0.16
Phenanthrene	2.7 x 10^{-8} ± 0.03	2.8 x 10^{-8} ± 0.03	1.3 x 10^{-8} ± 0.02
Anthracene	nd	3.3 x 10^{-10} ± 0.05	nd
Fluoranthene	2.8 x 10^{-8} ± 0.05	4.8 x 10^{-8} ± 0.04	4.1 x 10^{-8} ± 0.13
Pyrene	4.3 x 10^{-8} ± 0.04	5.1 x 10^{-8} ± 0.11	6.5 x 10^{-8} ± 0.50
Benzo(a)anthracene	1.7 x 10^{-8} ± 0.04	9.0 x 10^{-8} ± 0.32	3.8 x 10^{-8} ± 0.21
Chrysene	3.2 x 10^{-8} ± 0.05	3.4 x 10^{-8} ± 0.21	4.6 x 10^{-8} ± 0.25
Benzo(b)fluoranthene	7.1 x 10^{-9} ± 0.23	3.3 x 10^{-8} ± 0.12	1.6 x 10^{-8} ± 0.05
Benzo(k)fluoranthene	3.1 x 10^{-7} ± 0.12	1.2 x 10^{-8} ± 0.02	1.7 x 10^{-9} ± 0.08
Benzo(a)pyrene	nd	nd	nd
Dibenzo(a,h)anthracene	nd	nd	2.6 x 10^{-9} ± 0.16
Benzo(g,h,i)perylene	nd	nd	nd
Indeno[1,2,3-c,d]pyrene	nd	nd	nd

nd - not detected

PAHs. Higher contents of PAHs in the summer (July, Tables 1-3, Fig. 2) are probably caused by more intensive car traffic on the international route linking the eastern and western parts of Poland. Intensity of car traffic on this route can be estimate at about 5500 cars per day in the spring and some 8000 cars per day in the summer [20]. Higher intensity of summer traffic (at about 30 %) is in accordance with determined concentrations of PAHs in the investigated matrix. Comparison of the results obtained with reports of other authors [21-22] leads to the conclusion that medium values of PAHs in examined samples are comparable and are within permissible limits. Low standard deviation (under 5%) confirms good choice of procedures of isolation and determination of PAHs. The presence of these compounds in the environment and intensive increase of tumour diseases show a need for continuous control and monitoring of soil and of the whole ecosystem.

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