

# Soil Contamination with Polycyclic Aromatic Hydrocarbons (PAHs) in Poland - a Review

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## Abstract

The purpose of this paper is to provide a summary of data on PAH content in soils in Poland, published in literature over the last 20 years. This paper presents a preliminary assessment of soil contamination by PAHs for different land use patterns.

A review of available literature highlights the need to continue research on PAH contamination levels in environmental media in Poland, including surface soil. Results of such research would be important in order to better define exposure estimates in the general population and to examine the relationship between levels of PAHs in the environment and the subsequent development of health effects.

Keywords: PAHs, soil contamination, Poland, contaminated areas

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic chemicals consisting of two or more fused-benzene rings. PAHs are components of most fossil fuels and are ubiquitous in the natural environment [1, 2]. Natural sources include release in forest fires and from volcanic eruptions. Most environmental PAHs are products of incomplete combustion or pyrolysis of fossil fuels [1, 3, 4]. Stationary fuel sources are responsible for over 97% of PAH emissions [5]. Other important sources include automobile and truck emissions [6]. Hazardous waste sites can be a concentrated source of PAHs on a local scale. It is estimated that in Poland nearly 21 tons of one PAH alone, benzo(a)pyrene, are emitted into the air from especially burdensome industrial plants every year [7].

The study of these compounds is due mainly to their carcinogenic and widespread occurrence in environmental components, including surface soils. Most of the PAHs are introduced into soil from atmospheric deposition after local and long-range transport, which is supported by the presence of PAHs in soil of regions remote from any industrial activity [8]. Other potential sources of PAHs in soil include disposal from public sewage treatment, irrigation with coke oven effluent, leachate from bituminous coal storage sites,

and use of soil compost and fertilizers [9, 10, 11, 12, 13, 14].

Although PAHs are described as carcinogenic, only the following are considered as possible human or animal carcinogens [6]: benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene. The general population may be exposed to these compounds by inhalation of the compounds in tobacco smoke and contaminated air, as well as ingestion of contaminated food. Populations living in the vicinity of hazardous waste sites may be at greater risk of potential exposure to PAHs than the general population through inhalation, ingestion and direct contact with contaminated media [6].

Benzo(a)pyrene (BaP) is the most thoroughly studied of PAHs. Some PAHs are included in the "priority pollutants" lists developed by the United States Environmental Protection Agency (US EPA) and the European Community (EC). Some European countries have developed soil quality criteria for selected PAHs or their sum [15]. Critical limits for soil set in the Netherlands, Finland, Denmark, the United Kingdom, Belarussia, Moldavia, Russia and Ukraine are based on an effect-based approach: effects on ecosystem and/or effects on human beings.

## Level of Soil Contamination with PAHs - Results and Discussion

Analytical difficulties and lack of any standardized methods for determining polycyclic aromatic hydrocarbons in soil have caused few research institutions in Poland to investigate these compounds in soil. The studies have been carried out haphazardly and have usually covered rather not extensive areas. The studies of some larger areas concerned soil used for agricultural purposes in the Katowice, Lodz, Czestochowa, Lublin and north and eastern provinces [14, 16, 17, 18, 19, 20]. It should be emphasized that some results were obtained over ten or even twenty years ago using semiquantitative analytical methods [21, 22, 23, 24, 25]. The studies have often covered only the determination of benzo(a)pyrene [21, 25, 26]. The sum of PAHs under study regarded different kinds and numbers of compounds - from six [23] to sixteen numbers of compounds [14, 17, 18, 19, 27]. For these reasons interpreting results is very difficult or sometimes even impossible at all.

Tables 1 and 2 present data concerning the concentrations of PAHs in surface soil from uncontaminated and contaminated areas in Poland, respectively.

No soil quality values for PAHs have been established in Poland. The only recommendations on levels of some PAHs in soils exist in Poland, published by the Polish State

Environmental Inspectorate [28]. In fact, they are the requirements for remediation activity in Poland. Polish researchers have referred the results to the levels found in the unpolluted areas or reference values proposed in different countries. The "Dutch List" has been used most often for these purposes [29].

In the 1980's concentrations of from 25 to 30  $\mu\text{g}/\text{kg}$  were recognized as general "background" of soil contamination with BaP in Poland [25]. It was proposed to treat BaP content in soil from 300 to 1000  $\mu\text{g}/\text{kg}$  as high and above 1000  $\mu\text{g}/\text{kg}$  as very high soil contamination [25]. The Institute of Soil Science and Plant Cultivation in Pulawy proposed classification of agricultural soil contaminated with 16 PAHs [18]. According to this classification, PAH content in agricultural soil below 200  $\mu\text{g}/\text{kg}$  can be considered "background values". The sum of PAHs (600-10,000  $\mu\text{g}/\text{kg}$ ) corresponds to the contaminated soil with different levels of contamination and over 10,000  $\mu\text{g}/\text{kg}$  - corresponds to very high contaminated soils where reclamation is needed.

Concentrations of BaP in soil in clean regions of Poland ranged mostly from 2 to about 30  $\mu\text{g}/\text{kg}$  and seldom exceeded 70  $\mu\text{g}/\text{kg}$  (Table 1). The sum of PAHs found in uncontaminated soil in Poland in most cases did not exceed 600  $\mu\text{g}$ .

Soil contamination with PAHs increases considerably in industrial and urban areas (Table 2). PAH concentrations in

Table 1. PAH concentrations in uncontaminated soils.

| Place of sampling  | PAH concentrations ( $\mu\text{g}/\text{kg}$ ) |                  | Method of analysis                                    | References |
|--|--|------------------|---|------------|
|  | Sum  | BaP              |   |            |
| Rural areas Beskidy:<br>light sandy soil<br>heavy loamy soil   | –  | 1.5-6.5<br>50-78 | liquid column chromatography,<br>UV spectrophotometry | [22]       |
| Eastern and central<br>provinces                               | –  | 3.4-75           | TLC,<br>spectrofluorimetry                            | [25]       |
| Western regions of Poland                                      | –  | 25-30            | TLC,<br>spectrofluorimetry                            | [25]       |
| Szczawnica - Nowy Sącz<br>province                             | 58 <sup>a</sup>                                | –                | liquid column chromatography,<br>UV spectrophotometry | [23]       |
| Bierna - Bielsko-Biała<br>province                             | 71.3 <sup>b</sup>                              | 2.9              | liquid column chromatography,<br>UV spectrophotometry | [30]       |
| Miedzna (arable soils) - outskirts of<br>the Katowice province | 98-1038 <sup>c</sup><br>(M = 388)              | 2-77<br>(M = 29) | HPLC, UV detection                                    | [16]       |
| Białowieża - Białystok province                                | 190.3 <sup>c</sup>                             | 8.2              | HPLC, UV detection                                    | [16]       |
| Gogolin - Opole province                                       | 498.1 <sup>c</sup>                             | 21.0             | HPLC, UV detection                                    | [16]       |
| Wisła - Bielsko-Biała province                                 | 579.6 <sup>c</sup>                             | 37.4             | HPLC, UV detection                                    | [16]       |
| Martag - Elbląg province                                       | 317 <sup>c</sup>                               | 30.1             | HPLC, UV detection                                    | [16]       |
| Przewale - Zamość province                                     | 481.6 <sup>c</sup>                             | 16.0             | HPLC, UV detection                                    | [16]       |
| Agricultural soils in Poland                                   | G = 150 <sup>d</sup>                           | G = 15           | HPLC, UV detection                                    | [18]       |
| Wilków - Lublin province<br>(agricultural soils)               | 81-645<br>(M = 180) <sup>d</sup>               | –                | HPLC, UV detection                                    | [31]       |

Abbreviations and symbols - see below Table 2.

Table 2. PAH concentrations in contaminated soils.

| Place of sampling  | PAH concentrations<br>( $\mu\text{g}/\text{kg}$ ) |                          | Method of analysis                                    | References |
|--|---|--------------------------|---|------------|
|  | Sum   | BaP                      |   |            |
| 1  | 2   | 3                        | 4   | 5          |
| Surroundings of industrial plants  |   |                          |   |            |
| Vicinity of petrochemical complex, Płock   | –   | 11,000-15,000            | TLC,<br>UV spectrophotometry                          | [21]       |
| 5 km from petrochemical complex, Płock   | –   | < 2,000                  | TLC,<br>UV spectrophotometry                          | [21]       |
| 200 m from bituminous mass production plant  | –   | 734.6                    | TLC, spectrofluorimetry                               | [25]       |
| 300 m from chemical works  | –   | 515.4                    | TLC, spectrofluorimetry                               | [25]       |
| Coking plant, Zabrze town  | –   | 520-1,300                | liquid column chromatography,<br>UV spectrophotometry | [22]       |
| Areas under influence of coal mine and power plant "Turów"                             | –   | 1.1-580.0                | HPLC, UV detection                                    | [32]       |
| Protective zone around bituminous mass production plant - Strupiń Duży, Chełm province | 4,000-12,000 <sup>e</sup>                         | –                        | HPLC, UV detection                                    | [27]       |
| Lagoon soils - Czechowice Oil Refinery   | A = 31,140 <sup>f</sup>                           | 50-33,100<br>(A = 3,780) | HPLC, UV detection                                    | [33]       |
| Allotments   |   |                          |   |            |
| Zabrze town  | –   | 93.6-853.0               | liquid column chromatography,<br>UV spectrophotometry | [24]       |
| Kraków city  | 382-3,411 <sup>a</sup>                            | 60-337                   | liquid column chromatography,<br>UV spectrophotometry | [23]       |
| Bytom - Bobrek town  | –   | 1,000-2,600              | HPLC, UV detection                                    | [26]       |
| Agricultural soils   |   |                          |   |            |
| Bytom-Bobrek town  | –   | 400                      | HPLC, UV detection                                    | [26]       |
| Mysłowice region   | 65-2,913<br>(G = 264) <sup>e</sup>                | –                        | HPLC, UV detection                                    | [17]       |
| Tarnowskie Góry region   | 62-12,760<br>(M = 817) <sup>e</sup>               | –                        | HPLC, UV detection                                    | [14]       |
| Zabrze town  | 705-29,143<br>(M = 3,716) <sup>e</sup>            | 41-3,991<br>(M = 323)    | HPCL, UV detection                                    | [16]       |
| Sławków town   | 217-5,244<br>(M = 1,392) <sup>e</sup>             | 9-626<br>(M = 96)        | HPLC, UV detection                                    | [16]       |
| Łódź province  | 60-650<br>(M = 166) <sup>e</sup>                  | –                        | HPLC, UV detection                                    | [18]       |
| Częstochowa province   | M = 800 <sup>e</sup>                              | –                        | HPLC, UV detection                                    | [19]       |
| The proximity of the industrialised town Puławy - Lublin province                      | 70-2,787<br>(G = 217) <sup>d</sup>                | –                        | HPLC, UV detection                                    | [31]       |

| 1                                      | 2                          | 3          | 4   | 5    |
|--|----------------------------|------------|---|------|
| Soil contaminated by mobile sources    |                            |            |   |      |
| 150 m from engine-house                | –                          | 8,046      | TLC, spectrofluorimetry                               | [25] |
| Airport - 2 km from runway             | –                          | 456.7      | TLC, spectrofluorimetry                               | [25] |
| 100 m from heavy traffic road          | –                          | 11.4-13.4  | TLC, spectrofluorimetry                               | [25] |
| 50 m from heavy traffic road           | –                          | 19.3-23.6  |   |      |
| Road environs                          | ~ 5,000 <sup>b</sup>       | 500-600    | liquid column chromatography,<br>UV spectrophotometry | [22] |
| Vicinity of road (8,000 cars/day)      | –                          | 7.1-10.6   | Liquid column chromatography,<br>UV spectrophotometry | [34] |
| Vicinity of road                       | ~ 330-800 <sup>#</sup>     | 36.9-129.3 | GC  | [35] |
| Kraków city - heavy traffic roads side | 840-2,030 <sup>h</sup>     | 60-250     | HPLC, fluorescent detection                           | [36] |
| Industrial cities                      |                            |            |   |      |
| Upper Silesian Industrial Region       | ~ 2,800 <sup>b</sup>       | 400-980    | liquid column chromatography,<br>UV spectrophotometry | [22] |
| Gliwice town (Łabędy district)         | 1,085.1 <sup>b</sup>       | 150.75     | liquid column chromatography,<br>UV spectrophotometry | [30] |
| Zabrze town                            | 3,357-4,186 <sup>i</sup>   | 250-366    | HPLC, UV detection                                    | [37] |
| Łaziska town                           | 3,615-4,684 <sup>i</sup>   | 266-427    | HPLC, UV detection                                    | [37] |
| Katowice city                          | 11,994-12,194 <sup>i</sup> | 903-982    | HPLC, UV detection                                    | [37] |
| Bytom town                             | 7,246-7,905 <sup>i</sup>   | 406-455    | HPLC, UV detection                                    | [37] |

Abbreviations and symbols for Table 1 and 2:

PAH - polycyclic aromatic hydrocarbon

BaP - benzo(a)pyrene

GC - gas chromatography

HPLC - high performance liquid chromatography

TLC - thin layer chromatography

A - arithmetic mean

M - median

G - geometric mean

<sup>a</sup> - 6 PAHs: pyrene, fluoranthene, chrysene, benz(a)anthracene, benzo(a)pyrene, benzo(ghi)perylene

<sup>b</sup> - 10 PAHs: pyrene, fluoranthene, chrysene, benz(a)anthracene, benzo(e)pyrene, benzo(a)pyrene, benzo(ghi)perylene, perylene, anthanthrene, anthracene

<sup>c</sup> - 7 PAHs: fluoranthene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene

<sup>d</sup> - 13 PAHs: fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene

<sup>e</sup> - 16 PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene

<sup>f</sup> - 6 PAHs: fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene

<sup>g</sup> - 8 PAHs: fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(ghi)perylene, phenanthrene, perylene

<sup>h</sup> - 7 PAHs: phenanthrene, anthracene, pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene

<sup>i</sup> - PAHs: acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(a)pyrene, dibenz(ah)anthracene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene

soils effected by emission from anthropogenic sources are up to hundreds times higher than concentrations found in reference areas. The highest sum of PAH concentrations was reported in industrial soils at the lagoon located at the Czechowice Oil Refinery (mean - over 30,000 µg/kg) [33]. The maximum PAH concentration in agricultural soils reached 30,000 µg/kg [16]. In soils of contaminated areas higher contents of BaP were also found. Soil from industrial cities contained BaP levels tenfold higher than soil from reference areas. The maximum BaP concentration (33,100 µg/kg) [33], determined in industrial soil, was up to about one thousand times higher than its natural content. A review of literature allows only a preliminary assessment of soil contamination by PAHs in Poland, and points out that there is a need to continue research on PAH contamination levels in environmental media in Poland, including surface soil. Results of such research would be important in order to better define exposure estimates in the general population and to examine the relationship between levels of PAHs in the environment and the subsequent development of health effects. Especially, more information on PAH contamination of soil and plants grown in contaminated soil would be helpful in indentifying the risk for populations living at industrial sites. Establishing mandatory risk-based soil quality limits for PaHs and standardized analytical methods for their determination could be very useful for land management and would allow risk assessors to determine the potential and actual risk of soil contamination to man or the environment.

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