

## ACCUMULATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL

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**Abstract.** A study on the distribution and accumulation of polycyclic aromatic hydrocarbons (PAHs) was carried out in Tallinn, Pärnu, and two rural areas in Estonia. Thirteen PAHs listed as the priority pollutants by the US Environmental Protection Agency were identified in 102 soil samples (0–10 cm upper layer) collected in September 1996. The background PAH level in Estonian soil is estimated at 100–200 µg/kg dry weight. The corresponding PAH concentrations in the city of Tallinn were more than one order of magnitude higher. The PAH concentrations in the central part of Tallinn were significantly higher than in the outskirts of the city. The PAH concentrations in Pärnu were unexpectedly high. The predominant PAHs in all areas under study were pyrene, triphenylene, and fluoranthene. The ratio of 3–4 ring and 5–6 ring PAHs varied mainly from 3:1 to 5:1. PAH profiles indicate a variety of sources contaminating the soil of the cities.

**Key words:** polycyclic aromatic hydrocarbons, soil, contamination, cities, rural areas.

### INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs), a group of compounds composed of two or more fused aromatic rings, are wide-spread environmental pollutants. Most PAHs (and their heteroatomic derivatives) emitted into the environment come from anthropogenic sources. They are mainly formed as by-products of incomplete combustion of organic materials. PAHs have been identified in many emission sources, such as motor vehicle exhausts, power plants, chemical, coke, and

oil-shale industries, urban sewage. Primary natural sources of PAHs are forest fires and volcanic activity. The United States Environmental Protection Agency has identified 16 PAHs as the priority pollutants [1]. Eight of them are known to be possible or probable carcinogens. These are benzo(*a*)anthracene, chrysene, benzo(*k*)fluoranthene, benzo(*b*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-*cd*)pyrene, dibenzo(*ah*)anthracene, benzo(*ghi*)perylene. Bicyclic and tricyclic PAHs, which are more water-soluble than other PAHs, are not carcinogenic. PAH compounds convert into carcinogens through metabolic activation in the organism. In many circumstances the environmental occurrence of PAHs has been associated with adverse effects on public health [2].

PAHs are considered to be quite resistant to degradation. The existence of permanent pollution sources results in the accumulation of PAHs in soil, plants, and water bodies. The main factors that cause their degradation in the environment are solar radiation and biodegradation. Tetracyclic and, especially, higher molecular weight PAHs are considered to be quite resistant to degradation by microorganisms. On the other hand, it has been reported that higher molecular weight PAHs are rapidly transformed in water by the action of ultra-violet light. Soil contamination originates partly from PAH emissions into the atmosphere. Atmospheric PAHs reach the soil via deposition. Gaseous and particle-bound PAHs can be transported over long distances before deposition. PAHs are accumulated mainly in the humic layer of the soil. The PAH concentration in soil correlates significantly with the corresponding levels in the air [3], in the house dust [4], and in plants [5]. The PAH determination in soil is a convenient and effective method for the estimation of environmental pollution. The characteristic ratio of PAH and PAH profiles can be used in qualitative and quantitative source estimation [2, 3].

The main target of the present study was to assess the contamination of soil with PAHs in Estonia, to delimit corresponding PAH profiles in areas with different anthropogenic pollution load, and to determine the regional background soil pollution level by PAH. A study was carried out in areas with quite different anthropogenic pollution loads. The differences in the concentrations of PAHs in the soil and PAH profiles were determined in Tallinn, Pärnu, and two rural areas (Harjumaa and Pärnumaa). The figures for the rural areas were used for the estimation of the PAH background concentrations in the soil in Estonia.

## EXPERIMENTAL

A total of 102 soil samples (0–10 cm upper layer) were collected in September 1996 on dry days. Sampling density was 3–5 samples per 1 km<sup>2</sup> in the urban areas and 2 samples per 10 km<sup>2</sup> in the rural ones.

Samples were dried at 50°C and particles over 2 mm in size were removed from the sample. Dry samples of 20 g were soaked in 75 ml of hexane (analytical

grade, purified additionally with activated carbon) over night. The ultrasonic extraction procedure, twice á 5 min, followed (sonicator UZDA-A from Nauchpribor, USSR, operated at  $22 \pm 1.65$  kHz; the double amplitude at the tip of the standard horn of 15 mm was adjusted to 20 mm; the corresponding power input was 80 W). The second extraction was conducted with 50 ml of hexane. The joined hexane extracts were evaporated carefully to the volume of about 1 ml and then fractionated by thin-layer chromatography (TLC) with aluminium oxide (TLC grade, Reanal, Hungary). The mobile phase was hexane-benzene 4:1 (by volume). The PAH fraction was eluted twice á 5 ml with acetone (extra pure grade, Reachim, USSR). Acetone was evaporated dry at room temperature and the residue was dissolved in 0.2–2.0 ml of acetone (depending on PAH concentration). The PAH concentration was measured by means of high performance liquid chromatography (HPLC) (model 1311, Minsk, Belarus). As an eluting solvent acetonitrile-water (both HPLC grade) mixture 93:7 (by volume) with a flow rate  $8 \text{ ml min}^{-1}$  was used. Detection was fluorometric with initiation wavelength 254 and 298 nm and the range of registration 330–600 nm. The chromatographic column ( $0.5 \times 300$  mm) was filled with Silosorb C18 (Chemapol, Czechoslovakia). The coefficient of variation for the HPLC method was 1.5% [6]. The PAH standards were obtained from Aldrich Chemical Company. Thirteen PAHs, all listed as priority pollutants [1], were quantified in soil samples: phenanthrene (Ph), anthracene (A), fluoranthene (Fl), pyrene (P), triphenylene (TPh), benzo(a)anthracene (BaA), chrysene (Chr), benzo(e)pyrene + benzo(b)fluoranthene (BeP), perylene (Per), benzo(k)fluoranthene (BkFl), benzo(a)pyrene (BaP), and benzo(ghi)perylene (BghiPer). SPSS/PC+ software was used for statistical analysis of the data.

## RESULTS AND DISCUSSION

The data for different sampling sites are presented in the Table. The PAH concentrations in the soils of the city of Tallinn differed notably in different sampling points. They were significantly higher in the central part of the city (average value  $9015 \pm 6363 \text{ } \mu\text{g/kg}$  dry weight) than in the outskirts. Figure 1 illustrates the decline of the PAH concentration with increasing distance from the centre of the city.

The PAH concentrations in the soils of Pärnu were unexpectedly high (average value  $7665 \pm 4306 \text{ } \mu\text{g/kg}$  dry weight). They also showed, in general, a tendency to decrease from the centre of the town towards its outskirts. The average PAH pollution of soils in both cities, Tallinn and Pärnu, is quite high. One of the significant pollution sources may be motor vehicle exhausts. The data in the Table indicate that the PAH concentrations in the cities were an order of magnitude higher than in rural areas.

Content\* of polycyclic aromatic hydrocarbons (PAHs) in urban and rural soils, µg/kg dry weight

| PAH                                    | $\bar{x}$ | SD    | $x$ (max) | $x$ (min) |
|--|-----------|-------|-----------|-----------|
| Centre of the city of Tallinn, $n = 7$ |           |       |           |           |
| All                                    | 9 015     | 6 363 | 26 265    | 176       |
| Benzo(a)pyrene                         | 398       | 182   | 920       | 3.1       |
| 3-4 ring PAHs                          | 7 755     | 5 910 | 23 930    | 166.3     |
| 5 and more ring PAHs                   | 1 260     | 533   | 2 330     | 9.3       |
| City of Tallinn, $n = 34$              |           |       |           |           |
| All                                    | 2 241     | 1 396 | 26 265    | 68        |
| Benzo(a)pyrene                         | 105.6     | 60.4  | 920       | 3.1       |
| 3-4 ring PAHs                          | 1 890     | 980   | 23 934    | 17        |
| 5 and more ring PAHs                   | 351       | 150   | 2 330     | 0.1       |
| Town of Pärnu, $n = 16$                |           |       |           |           |
| All                                    | 7 665     | 4 306 | 42 000    | 168       |
| Benzo(a)pyrene                         | 1 113     | 313   | 12 600    | 8.8       |
| 3-4 ring PAHs                          | 5 720     | 3 440 | 27 980    | 144       |
| 5 and more ring PAHs                   | 1 945     | 922   | 14 010    | 95.1      |
| Harju County, $n = 37$                 |           |       |           |           |
| All                                    | 232       | 153   | 1 495     | 39.9      |
| Benzo(a)pyrene                         | 14.9      | 8.85  | 244       | 0.1       |
| 3-4 ring PAHs                          | 175       | 88    | 978       | 11.2      |
| 5 and more ring PAHs                   | 57.5      | 29    | 520       | 2.5       |
| Pärnu County, $n = 8$                  |           |       |           |           |
| All                                    | 584       | 379   | 1 100     | 271       |
| Benzo(a)pyrene                         | 26.9      | 13.6  | 73.9      | 10.5      |
| 3-4 ring PAHs                          | 488       | 390   | 1 072     | 151       |
| 5 and more ring PAHs                   | 96        | 90    | 219       | 28.8      |

\* $\bar{x}$ , mean concentration; SD, standard deviation of the mean;  $x$  (max), maximum concentration;  $x$  (min), minimum concentration.

One of the aims of the present study was to determine the regional background concentration of PAHs in soil in Estonia. The data obtained in two rural areas enable us to estimate the PAH background level in soil at 100–200 µg/kg dry weight. A comparison of these data with the corresponding data from other northern countries shows that they are somewhat lower than in South Norway and

about two times as high as in Central Norway [7]. The background levels in Estonia were also higher than the target value set by the Dutch government for unpolluted soil (20–50  $\mu\text{g}/\text{kg}$  dry weight) [8]. Note that a direct comparison of the data is impeded by differences in the composition of PAHs identified in these studies.

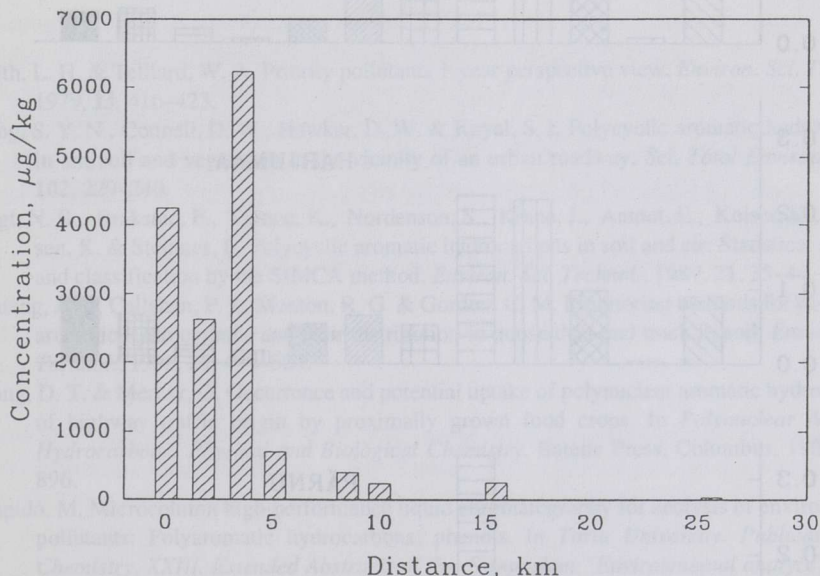


Fig. 1. PAH concentrations at various distances from the centre of the city of Tallinn (north-east direction).

The PAH profiles in different sampling areas are presented in Fig. 2. Three predominant components found in soil were pyrene, triphenylene, and fluoranthene in all areas studied. They formed 9–25, 20–25, and 10–25% of the total PAH content, respectively. The soil samples from Pärnu contained a relatively high amount (7–18%) of benzo(a)pyrene. In the other areas benzo(a)pyrene formed from 3.5 to 10% of the total PAH content. In all samples 3–4 ring PAHs prevailed and the ratio of 3–4 ring and 5–6 ring PAHs varied mainly from 3:1 to 5:1. PAH profiles indicate to a variety of PAH pollution sources contaminating soils of the cities.

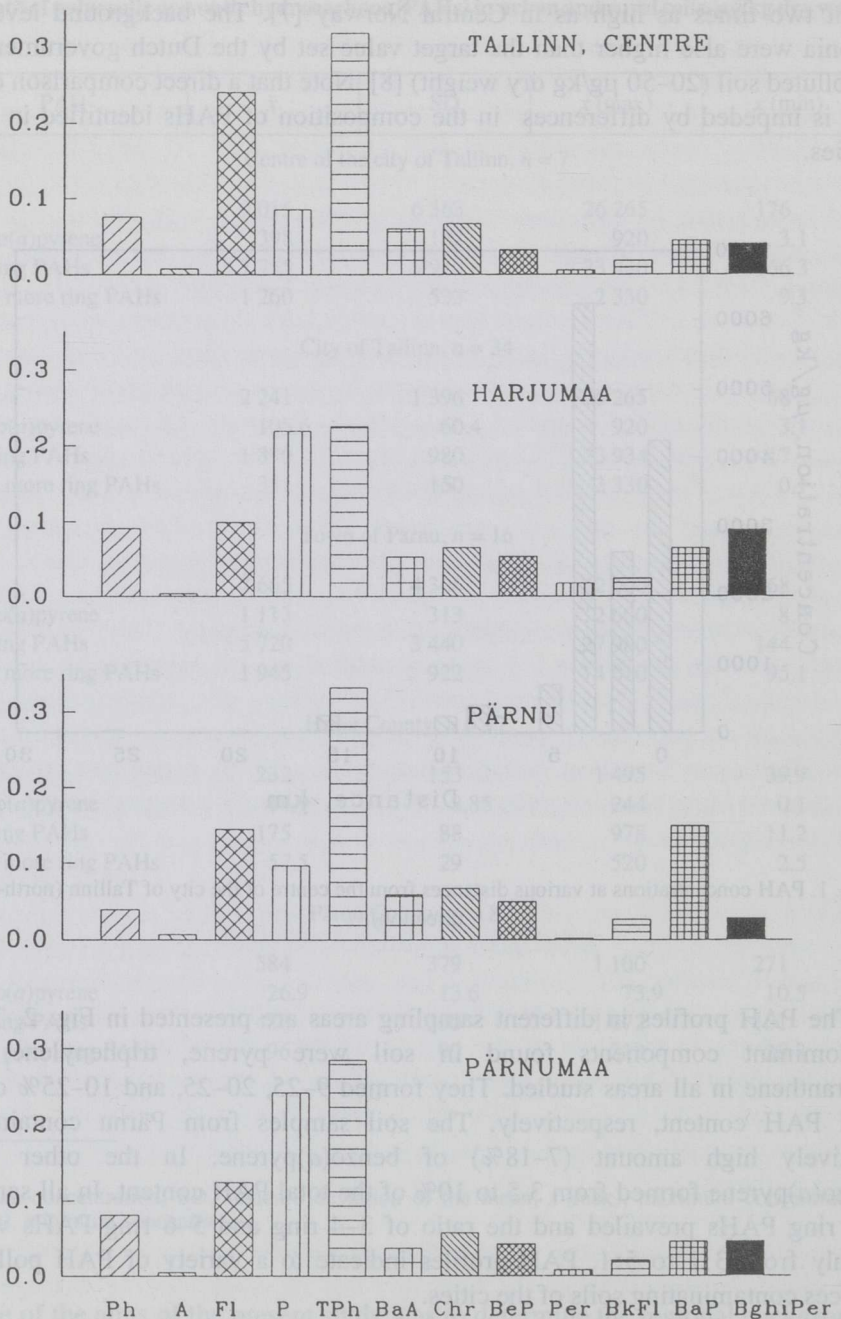


Fig. 2. Bar diagram of normalized average PAH concentrations for different sampling sites. Normalization was done by dividing the average concentration for each PAH by the summed concentration of all 13 PAHs in each sampling site. Refer to Experimental for abbreviations of PAHs.

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## PINNASE SAASTATUS POLÜTSÜKLILISTE AROMAATSETE SÜSIVESINIKEGA

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Polütsüklilised aromaatsed süsivesinikud (PAS) on põhiliselt antropogeense päritoluga. Uuringu eesmärk oli hinnata PAS-de jaotumust ja nende põhjustatud saastatust Eesti pinnastes. Proovid võeti 1996. aasta septembrikuu jooksul sademeteta päevadel Tallinnas, Pärnus ning maapiirkondades Harjumaal ja Pärnumaal. Maapiirkondade andmed võimaldavad määrata PAS-de fooni taset Eestis. Uuriti pealiskihti 10 cm sügavuseni kokku 102 proovi põhjal. Pinnaseproovides analüüsiiti 13 prioriteetsesse PAS-de nimekirja kuuluvat ühendit. Tallinna paikades võe-

tud pinnaseproovides olid PAS-de kontsentratsioonid väga erinevad. Kesklinnas olid need palju kõrgemad ja kahanesid äärelinna poole liikudes. Ka Pärnu linnas võetud proovides erinesid PAS-de sisaldused märgatavalt ning olid kesklinnas keskmiselt tunduvalt suuremad kui äärelinnas. Saadud tulemused viitavad suurele PAS-de saastekoormusele Tallinnas ja Pärnus. Üks olulisi saasteallikaid võiks olla nende linnade autotransport. Andmetest selgub, et linnades on pinna saastatus PAS-dega vähemalt üks suurusjärk kõrgem kui maapiirkondades. PAS-de regioonalne foon pinnases võiks olla 100–200 µg/kg kuivaines. PAS-de jaotumus piirkonniti oli üsnagi sarnane. Domineerivateks aineteks osutusid kõikides piirkondades püreen, trifenüleen ning fluoranteen. Üldiselt prevaleerisid pinnaseproovides 3–4-tuumalised PAS-d: 3–4- ning 5- ja enamatuumaliste PAS-de keskmine suhe oli eri kohtades 3:1 kuni 5:1. Pärnu linna proovides oli suhteliselt suur benzo(a)püreeni sisaldus. Üldiselt viitab PAS-de jaotumus linnaoludes saasteallikate mitmesusele.