Polycyclic aromatic hydrocarbon in urban soils of the Eastern European megalopolis: distribution, source identification and cancer risk evaluation

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Abstract

The study explores qualitative and quantitative composition of 15 priority PAHs in urban soils of some parkland, residential and industrial areas of the large industrial center in the Eastern Europe on example of Saint-Petersburg (Russian Federation). Aim of the study was to test the hypothesis on the PAH loading differences between urban territories with different land use scenarios. Qualitative and quantitative determination of PAHs in soils was carried out by reverse-phase high-performance liquid chromatography (HPLC). Benzo(a)pyrene toxic equivalency factors (TEFs) were used to estimate benzo(a)pyrene equivalent (BaPeq) concentrations in order to evaluate carcinogenic risk of soil contamination with PAHs. Results of the study demonstrated that soils within urban areas with different land utilization types are characterized by common loads of PAHs generally attributed to high traffic activity in the city. Considerable levels of soil contamination with PAHs were noted. Total PAH concentrations ranged from 0.33 to 8.10 mg·kg⁻¹ and showed no significant differences between land utilization types. The common tendency in PAH distribution patterns between investigated sites clearly indicates the common source of PAHs in urban soils. A larger portion of high molecular weight PAHs along with determined molecular ratios suggest the predominance of pyrogenic sources, mainly attributed to combustion of gasoline, diesel and oil. Petrogenic sources of PAHs have a significant portion as well defining the predominance of petroleum associated low molecular weight PAHs such as phenanthrene. Derived concentrations of 7 carcinogenic PAHs as well as calculated BaP total potency equivalents were multiple times higher than reported in a number of other studies, indicating a significant risk for human health in case of direct contact. The obtained BaPeq concentrations of the sum of 15 PAHs ranged from 0.05 to 1.39 mg·kg⁻¹. A vast majority of examined samples showed concentrations above the safe value of 0.6 mg·kg⁻¹ (CCME, 2010). One-way ANOVA results showed significant differences in levels of pyrene, fluoranthene and phenanthrene – the most abundant individual PAHs in examined sample, between parkland, residential and industrial land uses, suggesting the influence of land use factor on distribution of these pollutants. Exposure to these soils through direct contact probably poses a significant risk to human health from carcinogenic effects of PAHs, even in urban parklands.

1. Introduction

The quantity of toxic organic substances is extremely high, but in the world practice the evaluation of contamination levels of certain areas is produced mostly for polycyclic aromatic hydrocarbons (PAHs), an ubiquitous organic pollutants in environments, particularly in soils and sediments. PAHs are a large group of persistent organic compounds (POPs) consisting of several hundred individual homologues and isomers containing at least two condensed aromatic rings. Their input to the environment has both natural and anthropogenic origins. Natural sources includes releases from vegetation fires, diagenetic processes and volcanic exhalations (ATSDR 1995; Wickie 2000). In turn, anthropogenic PAHs occur from pyrolytic processes, especially incomplete combustion of organic during industrial activities, domestic heating, waste incineration, transportation and power generation (ATSDR 1995; Wickie 2000; Dyke et al. 2003). It is believed that by far most PAHs are released into environment by anthropogenic combustion of biomass and fossil fuels (Wickie 2000). Sign of anthropogenic contamination of soil with PAHs are even detected in such remote places as Antarctic Stations, which origin is doubted, whether it has natural sources, i.e. decomposition of plant and guano materials, or comes from anthropogenic sources, such as fuel combustion, petroleum products and long range transport with atmospheric solid particles (Abakumov et al. 2014; Abakumov et al. 2015). Some PAHs are of the most environmental importance because of the established carcinogenic, mutagenic and teratogenic effects in living organisms and in humans particularly (Menzie et al. 1992; Shaw and Connell 1994; Perera 1997; Yu 2002; Guo et al. 2013). A number of 16 PAHs have been listed as priority contaminants by both the US Environment Protection Agency (US EPA) and European Union (EU). Among them seven compounds, i.e. benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene are considered as probable human carcinogens (US EPA 2002). In Canada, US and some European countries normalization of soil contamination is provided upon developed soil quality criteria for selected PAHs or their sum. Only a few countries have established comprehensive soil guideline...
values (SGV) for particular land use at least for the sum 85 of priority PAHs (Σ7; 10; 15; 16). Generally, the
existing soil critical values provides only human health-risk based approaches and don’t consider protection of other
ecological receptors. In turn, US EPA has developed ecological soil screening levels (Eco-SSLs) for PAHs, which
are derived separately for four groups of ecological receptors: plants, soil invertebrates, birds and animals. However
these screening levels are intended to evaluate an unacceptable ecological risk to terrestrial receptors, they are not
designed to be used as cleanup levels. For this purpose US EPA adopted a human health based Preliminary
Remediation Goals for Soil (PRG) using estimates of different routes of exposure. In contrast to this, Russian
Federation has not yet developed soil guideline values at least for the sum of priority PAHs; normalization is
provided only for soil contamination with benzo(a)pyrene without distinction for particular land use. On top of that,
no threshold values are provided for other POPs. A summary of soil guideline values for PAHs set in some countries
is presented in supplementary materials 1. Thus studies on soil contamination with PAHs are of the most
importance as they provide information that can be further used to delineate special contaminated sites exhibiting
high risk to human exposure. Thousands of reports about PAHs concentrations, sources and health risk assessments
in urban and semirural areas from all over the world were published in recent years. Elevated levels of PAHs in
urban soils were reported in Hustan, USA (Hwang et al. 2002), Beijing, China (Tang et al. 2005), Glasgow of UK
and Torino of Italy (Morillo et al. 2007), and Esbjerg of Denmark (Essumang et al. 2011).

St. Petersburg is the largest industrial and transport center in the northwestern region of Russia and is of
great interest from the viewpoint of environmental concern. The ecological status of such a large center reflects the
whole range of socioeconomic problems resulting in decline of human health under the influence of various
chemical, physical and biological factors. The ecological situation in the city is determined by the emissions from
more than a thousand industrial enterprises, large railway junction, seaport and the great motor vehicle fleet – 1 670
794 cars and 207 975 trucks as of 2014 (Belousova et al. 2014). All this transport is served by a huge amount of
petrol stations and transport companies: currently in St. Petersburg operate 27 fuel operators and 397 petrol stations.
Industrial enterprises of the city include high-capacity, resource- and power-consuming ecologically dangerous
works. According to the data collected from the automatic air monitoring system of the city in 2014 total emission
into the air from both the stationary sources and vehicles has reached 513 200 t in 2014 of chemicals, including 16
903 t of hydrocarbons (CHx), 3000 t of black carbon (BC) and 47 900 t of volatile organic compounds (VOC)
(Belousova et al. 2014). The amount of emissions per capita complies 135.9 kg / year, per unit area – 434.5 t / km²
(Belousova et al. 2014). At the same time, 91.9% of emissions are accounted to the transport activity. Industrial and
transport emissions are the major source of soil contamination with PAHs in urban areas along with inputs from
petroleum products. No systematic survey of soil contamination with priority PAHs has been conducted yet in St.
Petersburg except for benzo(a)pyrene (Gorkiy and Petrova 2007). Considering this fact and environmental aspects
of the territory described above, St. Petersburg affords an excellent location to study geochemical cycles of PAHs.

Therefore this study is aimed to test the hypothesis on the PAH loading differences between urban
territories with different land use scenarios. The results of this study would contribute to the knowledge about PAH
distribution in urban soils of Eastern European region and may be used by decision makers during land
management.

Objectives of the study were to: 1) explore qualitative and quantitative composition of 15 priority PAHs in
urban soils in some parkland, residential and industrial areas of St. Petersburg; 2) compare with existing data on the
PAHs distribution in urban soils; 3) distinguish between PAHs sources using PAH molecular ratios; and 4) evaluate
cancer risks associated with soil contamination with PAHs within selected areas.

2. Materials and methods
2.1 Study site description

Choice of the study area, namely Primorsky, Vasilyevostrovsky and Kirovsky administrative Districts of St.
Petersburg was done in order of increasing of location density of potential stationary sources of contamination with
PAHs, population density and traffic activity. Detailed characteristics about each chosen area are given in Table 1.
Certain areas of recreational, residential and industrial land use scenarios within each chosen District were subjected
under the study. Information on the land use scenario of each chosen area was obtained using online map service
“Regional Geoinformational System RGIS” developed with the support of the Committee for land resources and
land management of St. Petersburg (Fig. 1). Potential sources of PAH contamination affecting PAH levels in soil
here are high traffic activity (Western highway and Primorsky prospect), steel and chemical industries (Kirovsky
engineering plant, Baltiysky shipyard plant, varnish factory “Kronos”), thermal-power-stations (“North-Western”).
Climate is moderately continental, significantly affected by the Baltic Sea. The average annual amount of precipitates varies 565-635 mm. Humidity factor – 1.1-1.3. The territory represents an almost flat plain with altitudes below 20 m above the sea level (Neva Lowland). Natural soil formation usually occurs on ancient lake-marine littoral sands, sandy loams, loams (less) depleted in calcium (Gararina et al. 2008). Urban soils are formed on the bulk deposits ranging from 0.9 to 4 m of thickness (Matinyan et al. 2005; Dashko et al. 2011). Soils are strongly disturbed by anthropogenic activities (buried, sealed and/or contaminated), with small relatively intact islands in natural and seminatural areas on the north, north-west and north-east of the City. Soils of the historical center are presented by anthropogenic soil-like formations called in national soil classification systems as “urbanozems” (Stroganova et al. 1992) or “ubiquozizems” (Shishov et al. 2006) and generally characterized by light grain size, modified soil profiles, with abundant inclusions of anthropogenic artefacts in the form of debris, domestic wastes and remains of communications, neutral to alkaline pH, high humus, nitrogen and phosphorus content, humate and fulvic-humate types of humus and traces of chemical contamination (Rusakov et al. 2005; Matinyan et al. 2005; Ufimtseva et al. 2011). Investigated urban soils were classified as Technosols according to the World Reference Base for soil resources (Micheli et al. 2006).

2.2 Sampling strategy and procedure

Sampling was conducted in September 2013 at 9 urban sites, in dry and clear weather conditions according to international standard protocol ISO 10381-1 (2002) and national sampling standard GOST 17.4.4.02-84 (1984). Soil samples were taken from 0-20 cm topsoil layer. A total of 135 grab soil samples were collected diagonally from 25 m² sampling plots were combined into 27 composite samples of 0.7 kg each one. Location of the sampling sites was defined according to proximity to residential areas and potential pollution sources (Fig.1).

Sampling strategy responds to the study objectives and is aimed to provide comprehensive characterization of the selected sites suspected to be contaminated with PAHs. Quantity of grab samples to be collected depended on the size of sampling sites, e.g., 15 grab samples per 0.8 ha site collected from sampling plots (S = 25 m²). Soil depth selected for sampling is a function of exposure routes (e.g., soil ingestion, dermal contact with soil and dust, inhalation of contaminated dust, inhalation of volatile compounds). Sampling pattern represents both the purposive judgement sampling techniques, delineating sample locations that assumed to be representative of the whole site and most contaminated. Instruments for sample derivation included stainless scoop and stainless knife prewashed with acetone. The representativeness of collected samples was provided thorough mixing and taking an average sample by quartering method.

Fig. 1. Location of the soil sampling sites.

<table>
<thead>
<tr>
<th>Land use</th>
<th>a - Primorskij District</th>
<th>b - Vasileostrovskij District</th>
<th>c - Kirovskij District</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parkland</td>
<td>1 - The park of the 300th anniversary of St. Petersburg, Primorskij prospect, 157. 59°59′2″ N, 30°11′33″ E.</td>
<td>4 - AkademicheskijGarden, 2d Line of Vasilyevskij Island, 2A. 59°56′19.8″ N, 30°17′18.3″ E.</td>
<td>7 - The park of 9th January, Stachek prospect, 19. 59°53′31.1″ N, 30°16′25.5″ E.</td>
</tr>
<tr>
<td></td>
<td>2 - Intersection of Yahtennaya street and Optikov street. 59°59′55.7″ N, 30°13′22.9″ E.</td>
<td>5 - Korablstroiteley street, 20, 19/2. 59°56′37.3″ N, 30°12′48.3″ E.</td>
<td>8 - Korneev street, 4. 59°53′06.9″ N, 30°16′03.8″ E.</td>
</tr>
<tr>
<td>Residential</td>
<td>3 - Vicinity of the Bus depot №2, Avtobusnaya street, 12A. 60°01′46.6″ N, 30°15′34.7″ E.</td>
<td>6 - Vicinity of the Baltic shipyard, Detskaya street, 3. 59°55′36.1″ N, 30°15′13.1″ E.</td>
<td>9 - Vicinity of the Kirovskij engineering plant, Stachek prospect, 47. 59°53′09.3″ N, 30°15′48.1″ E.</td>
</tr>
</tbody>
</table>

Collected samples were packed in labeled sterile plastic bags, kept in cool condition and transported to the laboratory. Once in laboratory, soil samples were dispersed on the sterile glass plates and air-dried at the room temperature for 5 days, cleaned from the organic and inorganic debris, grounded in laboratory vibrating cup mill, sieved through 0.25 mm caprone sieve and finally stored in the dark glass containers prewashed with acetone until analysis. This technique enables to prevent cross-contamination as well as losses of PAHs due to environmental factors (Berset et al. 1999).
2.3 HPLC, PAH source identification and risk evaluation

15 PAHs were analyzed, including naphthalene (NAP), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DBA), benzo(g,h,i)perylene (BPE), indeno(1,2,3-cd)pyrene (IPy) (Fig. 2).

Fig. 2. Structures of the studied PAH compounds

PAHs content in samples were determined on the basis of US EPA method 8310 (1996c), national standard method PND F 16.1:2:2.3:62-09 (2009), and Gabov (2007; 2008). Extraction of the PAHs was carried out at room temperature with methylene chloride (high purity grade) and ultrasonic treatment via Branson 3510 ultrasonic bath (USA, power 469 W, working frequency 42 kHz) following the US EPA method 3550b (1996c). Solvent removal (evaporation) was carried out with Kuderna–Danish concentrator (Supelco). PAHs fractions were purified by consecutive chromatography in columns filled with aluminum oxide (Brockman activity grade 2-3, Neva Reactive) and silica gel (Fluka) according to the US EPA purification method 3600c (1996d). The purity was controlled by the absence of peaks in the blank chromatogram. A standard mixture of 15 PAHs (Supelco) with the concentrations of each component in the range of 100–2000 ng/cm² was used to prepare the standard PAH solutions. Qualitative and quantitative determination of PAHs in soils was carried out by reverse-phase high-performance liquid chromatography (HPLC) in gradient mode with spectrofluorimetric detection via chromatograph "Lyumanrom" ("Lumex", Russia). Chromatography was performed at 30°C on a column Supelec™ LC-PAH n5 μm (25 cm × 2.1 mm). Mobile phase was provided with acetonitrile-water gradient. Samples of 10 μl volume were injected using an injection valve. Individual PAHs were identified by the time of retention and comparison of fluorescence spectra of the components coming from the column with spectra of the standard PAHs. Quantitative analysis of PAHs was performed by external standard method. For the quality assurance purposes Standard reference materials® 1944 New York/New Jersey Waterway Sediment (National Institute of Standards and Technologies NIST, USA) containing a mixture of 15 PAHs were subjected to the procedure described above. The error of measuring the PAHs (benz[a]pyrene) in the soils was 3% in the range of 5–40 ng/g and 25% in the range of 40–2000 ng/g with a confidence probability of P = 0.95.

PAH molecular markers and ratios were used to determine PAH sources (Pandey et al. 1999; Yunker et al. 2002; Hwang et al. 2003). Sum of combustion PAHs (CombPAH/15PAH) was used as tracer of pyrogenic sources. CombPAH/15PAH marker indicates portion of the sum of combustion specific compounds in total PAH content, which are Fluoranthen, Pyrene, Chrysene, Benzo(a)anthracene, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene (Prah et Carpenter, 1983). Applied PAH molecular markers and ratios as well as their ranges are given in supplementary materials 2.

Since benzo[a]pyrene (BaP) is the most studied PAH, the carcinogenic potential of other PAHs is generally assessed referring to it that of BaP (“toxicity equivalence factors” (TEFs), in similar way to the “toxic equivalents” (TEQ) used in the evaluation of the toxicity of dioxins and furans. Benzo[a]pyrene Potency Equivalence Approach is a major approach used by regulatory agencies such as the US EPA (1993; 1999), California EPA (OEHHA 1992), Netherlands (Verbruggen et al. 2001), the UK (Duggan and Strehlow 1995), or Provinces of British Columbia and Ontario for assessing the human health risks of PAH-containing mixtures.

2.4 Soil properties analysis and statistical treatment

Total organic carbon (TOC) was determined using a “Leco” CHN-628 elemental analyzer (USA, combustion temperature 1030 °C, oxygen boost time 28 s). Inorganic carbonates were removed before analysis by acidification in situ of the grounded samples with 1 M hydrochloric acid in order to avoid uncertainty in TOC determination. Clay content was determined using laser diffractometer “Shimadzu” SALD-2201 (Japan). All measurements were done in triplicate. All measurements were converted to absolutely dry sample. Data on analyzed properties of the studied soils is presented in Table 2.

Measured TOC concentrations in studied samples ranged between 3.82 to 6.41% with a median value of 4.80%. Numerous studies suggested that soil organic matter (SOM) content plays an important role in retention of PAH in soil (Conse et al. 2001; Chung and Alexander 2002). In simple terms the higher SOM concentrations are, than the higher amount of PAHs can be absorbed (Karakishof and Brown, 1979; Wöcke, 2000). Entering the soil from the atmosphere PAHs are preferentially sorbed to aggregate surfaces (Wöcke, 1996). The close association of PAHs with SOM results in differentiation of organic contaminants pools among particle-size fractions (Guggenberger et al. 1996). A significant increase of PAH concentrations in finer fractions is shown in a number of
studies (Wilcke, 1996). Clay content in studied soils ranges between 1.87 and 8.50 %. A correlation coefficients were calculated in present study in order to reveal relationship between levels of PAH in soil and analyzed soil parameters. A strong positive correlation was found between sum of 15 PAH in soil and clay content \( r = 0.91; n = 27; p = 0.95 \), however, no correlation of total PAH and TOC concentrations in soil was detected.

Statistical treatment of the data was carried out with STATISTICA 10.0 software. One-way ANOVA was applied in order to test statistical significance of differences between obtained data. The essence of the method is based on estimation of the significance of averages differences between three or more independent groups of data combined by one feature (factor). The null hypothesis of the averages equality is tested during the analysis suggesting the provisions on the equality or inequality of variances. In case of rejection of null hypothesis basic analysis is not applicable. If the variances are equal, F-test Fisher criterion is used for evaluation of intergroup and intragroup variability. If F-statistics exceeds the critical value, the null hypothesis is rejected considering inequality of averages. Post-hoc-test (Fisher LSD) was used to provide detailed evaluation of averages differences between analyzed groups of data. A feature of post-hoc-test is application of intra-group mean squares for the assessment of any pair averages. Differences were considered to be significant at the 95% confidence level. All calculations were carried out via STATISTICA 10.0 software. PAH concentrations were analyzed at least in triplicate. Calculated mean concentrations were provided with standard deviations \( (a \pm b) \).

3. Results and discussion

3.1 PAH concentrations in studied soils

The levels of 15 individual PAH compounds analyzed in soils are shown in Table 3. The sum of 15 PAH and the sum of 7 compounds included in the group of probable human carcinogens (B2) by the US EPA (1993) are given additionally. Total PAH concentrations in studied soils were found to range from traces to 8.06 mg·kg\(^{-1}\) (sum of 15 priority PAH, hereafter referred to 15PAH). The vast majority of samples were characterized by concentrations of more than 1 mg·kg\(^{-1}\), which is set as a guide level for total PAH content in soil by a number of countries. The highest 15PAH levels were observed in soil samples collected from residential and industrial sites reaching an average of 4.19 and 4.01 mg·kg\(^{-1}\) respectively with a maximal value of 8.06 mg·kg\(^{-1}\) for industrial site in Kirovsky district (hereafter – K.D.). Concentrations found in parkland areas were substantially lower than those of residential and industrial, with an average value of 1.08 mg·kg\(^{-1}\).

Distribution of the sum of 7 carcinogenic PAH (7PAH) in soils of the studied urban sites is generally characterized by the same pattern as the total PAH content in soils. The highest 7PAH levels were measured in soil samples taken from residential sites (1.94 mg·kg\(^{-1}\)) with an absolute value of 3.47 mg·kg\(^{-1}\) in technosol of K.D. residential area. 7PAH levels in parkland areas tend to be at lower range respectively to distribution of 15PAH. All sampling sites were located in a proximity of less than 250 m to the highways (Korablstroiteley street, Stachek prospect, Optikov prospect, University embankment, Bolshoi prospect V.O. and others) showing heavy traffic. The portion of 7PAH to the 15PAH in all tested samples ranged between 41 % and 46 %, which evidently shows that the soils may represent considerable health risk for human.

The bar chart showing the contribution of PAH with different ring numbers to the sum of PAH in soils is depicted in Fig. 3. The sum of organic pollutants is mostly dominated by heavy molecular weight PAH with 4-5 rings. Portion of 4-ringed PAH compounds in soil of residential and industrial sites accounts for 50% of the sum decreasing to 34% in parkland soils. 5 ringed PAH including such compounds as BaP, BbF, BkF, and DBA contribute up to 31 % of the sum of 15PAH insignificantly varying between studied areas. The rest portion is accounted for the 6-ringed (10-14%) and low molecular weight PAHs with 2 or 3 rings in structure (11-17%).

Fig 3. Distribution pattern of PAHs with different ring numbers in studied soils

The pie chart illustrating composition of PAH mixtures in soils is depicted in Fig. 4. The obvious equality in PAH distribution patterns in all studied sites clearly indicates the common source of PAHs. Pyrene and Fluoranthene (4-ring PAHs) are the most abundant compounds in examined samples, portion of which accounts for 16-18 % of 15PAH. The following predominant compounds are 5-ring PAH benzo(b)fluoranthene (10-11%) and benzo(a)pyrene (8-11%). The rest portion of the sum is represented by lighter weight PAHs (2-3-ring PAHs) and is generally dominated by Phenanthrene (6-9%). Domination of 4 and 5-ring PAHs, mainly PYR, FLT, BbF and BaP, in studied soils is indicative of elevated diesel fuel consumption activity on the territory. Estimated diesel consumption in St. Petersburg reaches 38% of the total fuel use for transportation (Belousova et al. 2014). As known emission rate of heavy weight PAH fraction due to diesel combustion is several times higher (Sjogren et al. 1996; Marr et al. 1999).
The main anthropogenic impact on the studied territories is the intensive monitoring systems may be applied in different land utilization types. The described distribution patterns of individual PAHs are similar to those of this study: the most abundant are 4-5 ring PAHs, particularly Pyrene (17%), Fluoranthene (17%), Benzo(a)anthracene (13%), Benzo(b)fluoranthene (12%) and Benzo(a)pyrene (12%). Several PAHs were noticed to exhibit higher contents of heavy polycyclic natural origin, as both of the samples were represented by fresh organic material (peat) which is used as amendment in soils of residential areas and roadsides. Thus the findings of above mentioned study suggest that spatial distribution of PAHs is mainly dictated by the closeness to highways and by the artificial input of peat material in the urban soils.

Fig 4. Composition of PAH mixtures in studied soils

Obtained data are nearly consistent with data from Lodygin et al. (2008) in soils of Vasilievsky Island in St. Petersburg. The main anthropogenic impact on soils of residential area of the island was exerted by light polyaromatics, including 2-4 ring substances (as stated by the author), the portion of which in the total content of PAHs was more than 50%. Maximum concentrations of PAHs were detected in soils along highways with intense traffic and considerable emission of combustion gases. The reported total PAH content ranged from 0.197 to 8.20 mg·kg$^{-1}$ between different land utilization types. The described distribution patterns of individual PAHs are similar to those of this study: the most abundant are 4-5 ring PAHs, particularly Pyrene (17%), Fluoranthene (17%), Benzo(a)anthracene (13%), Benzo(b)fluoranthene (12%) and Benzo(a)pyrene (12%). Several samples were noticed to exhibit higher contents of heavy polycyclic natural origin, as both of the samples were represented by fresh organic material (peat) which is used as amendment in soils of residential areas and roadsides. Thus the findings of above mentioned study suggest that spatial distribution of PAHs is mainly dictated by the closeness to highways and by the artificial input of peat material in the urban soils.

There is still a lack of information about PAHs concentrations in soils of St. Petersburg, so the data on the pollutants distribution in water sediments obtained from environmental monitoring systems may be applied in discussion for evaluation of the PAH loads. Comparative PAH levels were detected in bottom sediments in different parts of Neva Bay (Gulf of Finland) and along the Niva river waterway. Reported total PAHs concentrations ranged between 0.01 to 14.5 mg·kg$^{-1}$ (HELCOM 2014). Benzo(a)pyrene was detected in 96% of sediment samples taken with and average concentration of 0.09 mg·kg$^{-1}$.

Total PAH concentrations in soils of urban and industrial sites from a number of investigations set in other countries are summarized in Table 4. Tang et al. (2005) reported a sum of 16 PAHs of 27.82 mg·kg$^{-1}$ in roadside soils of Beijing, China. Hwang et al. (2002) found a total PAH concentration of 0.20-2.20 mg·kg$^{-1}$ in urban and suburban soils in Huston, Texas, USA. Notable PAH concentrations were observed by Mielke et al. (2001) in New Orleans urban soils (USA), fluctuating around a medium level of 3.73 mg·kg$^{-1}$. Nadal et al. (2004) reported relatively lower 16 PAHs levels in soils of the vicinity of the chemical and petrochemical industries and urban/residential sites in Tarragona County (Catalonia, Spain), ranging 284 between 0.11 and 1.0 mg·kg$^{-1}$.

Comparable findings were announced by Bucheli et al. (2004) for soils of urban and semirural areas in Switzerland, containing 0.05-0.62 mg·kg$^{-1}$ of the sum of 16 PAHs. In general terms, the predominance of 3-5 ring PAHs is noted, which is mainly attributed with influence of the anthropogenic activities on the studied territories.

3.2 Determination of the PAH sources and statistics

While a domination of high molecular weight PAH fraction indicates a combustion origin (pyrogenic), enrichment of low molecular weight PAHs is common in fresh fuels (petrogenic) (Mask et al. 1987, Budzinski et al. 1997). Special molecular markers and ratios, proposed by Yunker et al. (2002) and a total combustion PAHs index, reported by Hwang et al. (2003) were applied for PAH sources apportionment. Obtained meanings of applied PAH molecular ratios are listed in Table 5. Applied markers allow to distinguish between pyrogenic and petrogenic as well as traffic and non-traffic sources of PAHs, namely: ANT/(ANT+PHE), FLT/(FLT+PYR), BaA/(BaA+CHR), IPY/IPY+BPE, CombPAH/15PAH and BaP/BPE. Calculated ratios for samples taken from residential and industrial exhibited numbers that point to a domination of pyrogenically formed PAHs. The cross-plots of the PAH ratios is depicted in Fig. 5.

Fig. 5 PAH source apportionment

Several markers are indicative of certain combustion sources of PAHs, appointing to gasoline, diesel, crude oil or grass, coal and wood combustion origins, namely: FLT/(FLT+PYR), BaA/(BaA+CHR), IPY/IPY+BPE and BaP/BPE. The calculated FLT/(FLT+PYR) (0.49-0.51), IPY/IPY+BPE (0.30-0.40) and BaP/BPE (1.20-1.64) values point to a domination of gasoline, diesel and oil combustion. However, obtained values of FLT/(FLT+PYR) and BaA/(BaA+CHR) ratios suggested that coal and wood combustion have a certain role in PAHs origination as well. It is important to note that the shift of heavy and low molecular PAHs ratio towards the heavy ones cannot be explained only by anthropogenic factor, the degradation of lighter PAHs due to environmental factors such as photolysis under the direct sun rays in the topsoil layers, as well as thermal degradation, biological uptake and biodegradation may play a significant role as well (Behymer and Hites 1985; Wild and Jones 1995; Wang 1998; Johnsen 2005; Choi et al. 2010). These processes are predetermined by physical and chemical properties of the lighter fraction PAHs such as low molecular weight, high vapor pressure and high volatility rate (Mackay and Hickie 2000). Volatilization was proved to play the most significant role in the global degradation of the 2- and 3-
ringed PAHs especially. Park et al. (1990) reported that approximately 30% loss of Naphthalene accounts for 
volatilization, while for the remaining compounds this process was insignificant. Heavy weight PAHs, i.e. 4-6-ring 
compounds, have low solubility in water and low volatility, strong affinity to particulates (BC and SOM, fine 
fractions), are less accessible for biological uptake and degradation and thus are more persistent in the environment 
(Johnsen 2005; Haritash 2009). It has been proven that PAHs may form nonextractable \([14C]PAH\) residues in soil 
under the stimulation of microbial activity, which obviously leads to unexpected lower results while analyzing the 
concentrations of Naphthalene, Anthracene, Pyrene and Benzo(a)pyrene in soil samples (Eschenbach et al. 1994; 
Eschenbach et al. 1998).

Obtained probabilities for One-way ANOVA revealed no statistically significant differences of total PAH 
concentrations in soils between different land uses \((P < 0.05)\). Plot of LS Means is depicted in Fig. 6.

Fig. 6. LS Means plot, differences of PAH levels in soil between land uses.

The differences in levels of individual PAH compounds were tested using Post-hoc Fisher LSD test. The 
results showed significant differences of FLT, PYR and PHE concentrations between parkland, residential and 
industrial areas \((p = 0.01-0.03)\). The tested hypothesis suggested that PAH levels in urban soil may differ between 
areas with different land utilization type, following the order: industrial, residential, parkland. Thus the results of the 
study did not prove the tested hypothesis, suggesting the argument of equal PAHs load on the urban soils. The land 
use factor is expressed only in distribution of the dominant individual PAHs, particularly FLT and PYR. These 
compounds are known to be a part of the PAHs mixtures isolated from the exhaust gases and industrial emissions 
(Fernandes et al. 1997; Rehwagen et al. 2005). So not too surprising, that elevated levels of these pollutants are 
expected primarily in industrial and transport areas along with surroundings, where maximum input of black carbon 
from air pollution sources is noted. PHE representing low molecular weight PAH is a thermodynamically stable tri-

aromatic compound arising from petroleum-hydrocarbon-based releases. Distribution of this contaminant follows 
the scheme of potential sources of contamination with petroleum products allocation (Fig. 7).

Fig. 7. Scale of potential sources of contamination with petroleum products (units per square km) with PHE 
distribution plots.

3.3 Risk evaluation of PAHs in soils

Health risk associated with soil contamination with PAHs was assessed using benzo(a)pyrene total potency 
equivalents approach \((\text{BaP}_{eq})\). The \(\text{BaP}_{eq}\) for a soil sample is simply calculated by multiplying the concentration of 
each PAH in the sample by its benzo(a)pyrene toxic equivalency factor \((\text{TEF})\), given in Table 6.

The calculated \(\text{BaP}_{eq}\) on the average concentration of 15PAH (here and after referred to \(\text{BaP}_{eq}-15\text{PAH}\)) 
varied between 0.44 to 0.66 mg kg\(^{-1}\) dry soil. The highest \(\text{BaP}_{eq}-15\text{PAH}\) mean concentrations were found in 
residential and industrial areas – 0.66 and 0.55 mg kg\(^{-1}\) respectively. Parkland areas are characterized by the lower 
but still considerable levels of \(\text{BaP}_{eq}-15\text{PAH}\) (mean 0.44 mg kg\(^{-1}\)). It is to be noted that one single sample taken 
from the Kiryovskij parkland exhibited a total \(\text{BaP}_{eq}\) concentration of 1.84 mg kg\(^{-1}\) (The park of 9th January), which 
evidently shows that parkland land uses are subjected under a high load of PAHs as well as other land uses. 
Obtained values are several times higher than reported total PAHs carcinogenic potencies in a number of studies 
\((\text{BaP}_{eq} \text{of total PAHs): 0.02 mg kg}^{-1} \text{ in soils of Viseu and 0.23 mg kg}^{-1} \text{ in Lisbon, Portugal (Cachada et al. 2012); 
Nadal et al. (2004) reported BaP}_{eq} \text{ concentrations varying between 0.02 to 0.12 mg kg}^{-1} \text{ in soils of Tarragona 
County, Spain; 0.18 mg kg}^{-1}\text{ in soils of Beijing and 0.24 mg kg}^{-1} \text{ in Shanghai, China (Lu et al. 2010; Wang et al. 
2013).}

Finally, obtained \(\text{BaP} \text{total potency equivalents of PAHs were compared with Soil Quality Guideline values 
for the direct contact with contaminated soil in respect to particular land use (CCME 2010), setting out the 
acceptable level of incremental lifetime cancer risk (ILCR) of }1 \times 10^{-6}\text{ for }\text{BaP}_{eq}\text{ concentration in soil above the 0.6 
to 5.3 mg kg}^{-1}\text{ (for each land use). The reported }\text{BaP}_{eq}\text{ for mean total PAH concentrations were above the safe level 
of 0.6 mg kg}^{-1}\text{. Exposure to these soils through direct contact probably poses a significant risk to human health from 
carcinogenic effects of PAHs, even in urban parklands.}

4. Conclusions

Results of the study demonstrated that soils within urban areas with different land utilization types are 
characterized by common loads of PAHs generally attributed to high traffic density of the city. Considerable levels 
of soil contamination with PAHs were noted. The common tendency in PAH distribution patterns between 
investigated sites clearly indicates the common source of PAHs in urban soils. A larger portion of high molecular 
weight PAHs along with determined molecular ratios suggest the predominance of pyrogenic sources, mainly
attributed to combustion of gasoline, diesel and oil. Petrogenic sources of PAHs have a significant portion as well
defining the predominance of petroleum associated low molecular weight PAHs such as phenanthrene. Derived
concentrations of 7 carcinogenic PAHs as well as calculated BaP total potency equivalents were multiple times
higher than reported in a number of other studies, indicating a significant risk for human health in case of direct
contact. One-way ANOVA results showed significant differences in levels of pyrene, fluoranthene and
phenanthrene – the most abundant individual PAHs in examined sampled, between parkland, residential and
industrial land uses, suggesting the influence of land use factor on distribution of these pollutants. Further study with
an application of complex statistical methods is needed such as principal component analysis which would
contribute to precision of PAHs sources allocation.

Acknowledgments
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2015.
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September 2015.
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hydrocarbons in soils induced by soil treatment with humic substances. Environmental pollution, 112(1),
27-31.
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geological conditions of St. Petersburg. Journal of Urban development and Geotechnical Engineering
for Humans: Benzo[a]pyrene. Department for Environment, Food and Rural Affairs and the Environment


Table 1. Description of the study area

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Units</th>
<th>Primorsky District</th>
<th>Vasileostrovsky District</th>
<th>Kirovsky District</th>
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<tbody>
<tr>
<td>S</td>
<td>km²</td>
<td>109.87</td>
<td>17.1</td>
<td>47.10</td>
</tr>
<tr>
<td>Population</td>
<td>-</td>
<td>534 646</td>
<td>211 048</td>
<td>334 746</td>
</tr>
<tr>
<td>Industries</td>
<td>units</td>
<td>250</td>
<td>350</td>
<td>70</td>
</tr>
<tr>
<td>Number of potential contamination sources with petroleum products</td>
<td>units</td>
<td>14</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Density of potential contamination sources</td>
<td>units per km²</td>
<td>0.13</td>
<td>0.41</td>
<td>0.21</td>
</tr>
<tr>
<td>CH₄ emissions from stationary sources in 2014</td>
<td>thousand tons</td>
<td>0.556</td>
<td>0.034</td>
<td>0.708</td>
</tr>
<tr>
<td>VOC emissions from stationary sources in 2014</td>
<td>thousand tons</td>
<td>0.153</td>
<td>0.099</td>
<td>0.545</td>
</tr>
<tr>
<td>BC emissions from stationary sources in 2014</td>
<td>thousand tons</td>
<td>0.237</td>
<td>0.037</td>
<td>0.174</td>
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</table>

Table 2. Physicochemical properties of the studied soils

<table>
<thead>
<tr>
<th>District</th>
<th>Land use</th>
<th>Soil type. FAO</th>
<th>TOC</th>
<th>Clay</th>
</tr>
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<tr>
<td>Primorskiy</td>
<td>Parkland</td>
<td>Mollie Technosol</td>
<td>4.10 ± 0.01</td>
<td>5.83 ± 0.21</td>
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<tr>
<td></td>
<td>Residential</td>
<td>Urbic Technosol</td>
<td>3.82 ± 0.03</td>
<td>7.43 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>Urbic Technosol</td>
<td>5.49 ± 0.02</td>
<td>8.50 ± 0.10</td>
</tr>
<tr>
<td>Vasileostrovski</td>
<td>Parkland</td>
<td>Mollie Technosol</td>
<td>5.39 ± 0.01</td>
<td>7.3 ± 0.20</td>
</tr>
<tr>
<td></td>
<td>Residential</td>
<td>Urbic Technosol</td>
<td>6.41 ± 0.02</td>
<td>1.87 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>Urbic Technosol</td>
<td>5.28 ± 0.02</td>
<td>3.27 ± 0.15</td>
</tr>
<tr>
<td>Kirovskij</td>
<td>Parkland</td>
<td>Mollie Technosol</td>
<td>4.19 ± 0.03</td>
<td>7.5 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>Residential</td>
<td>Urbic Technosol</td>
<td>4.80 ± 0.03</td>
<td>3.27 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>Industrial</td>
<td>Urbic Technosol</td>
<td>3.09 ± 0.02</td>
<td>7.67 ± 0.06</td>
</tr>
</tbody>
</table>
Table 3. PAH mean concentrations in soils of St. Petersburg (mg·kg⁻¹).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parkland (n = 9)</th>
<th>Residential (n = 9)</th>
<th>Industrial (n = 9)</th>
<th>P One-way ANOVA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean ± SD</td>
<td>Max</td>
<td>Min</td>
<td>Mean ± SD</td>
</tr>
<tr>
<td>NAP</td>
<td>0.06 ± 0.08</td>
<td>0.28</td>
<td>0.03</td>
<td>0.05 ± 0.02</td>
</tr>
<tr>
<td>ANA</td>
<td>0.02 ± 0.06</td>
<td>0.18</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FLU</td>
<td>0.10 ± 0.06</td>
<td>0.23</td>
<td>0.05</td>
<td>0.17 ± 0.11</td>
</tr>
<tr>
<td>PHE</td>
<td>0.16 ± 0.13</td>
<td>0.45</td>
<td>0.05</td>
<td>0.26 ± 0.17</td>
</tr>
<tr>
<td>ANT</td>
<td>0.06 ± 0.11</td>
<td>0.37</td>
<td>0.01</td>
<td>0.04 ± 0.04</td>
</tr>
<tr>
<td>FLT</td>
<td>0.18 ± 0.07</td>
<td>0.35</td>
<td>0.09</td>
<td>0.69 ± 0.52</td>
</tr>
<tr>
<td>PYR</td>
<td>0.18 ± 0.08</td>
<td>0.35</td>
<td>0.09</td>
<td>0.74 ± 0.55</td>
</tr>
<tr>
<td>BaA</td>
<td>0.19 ± 0.17</td>
<td>0.53</td>
<td>0.04</td>
<td>0.35 ± 0.26</td>
</tr>
<tr>
<td>CHR</td>
<td>0.15 ± 0.14</td>
<td>0.44</td>
<td>0.01</td>
<td>0.31 ± 0.24</td>
</tr>
<tr>
<td>BBF</td>
<td>0.23 ± 0.21</td>
<td>0.69</td>
<td>0.05</td>
<td>0.46 ± 0.30</td>
</tr>
<tr>
<td>BKF</td>
<td>0.15 ± 0.17</td>
<td>0.56</td>
<td>0.02</td>
<td>0.19 ± 0.14</td>
</tr>
<tr>
<td>BaP</td>
<td>0.22 ± 0.22</td>
<td>0.70</td>
<td>0.04</td>
<td>0.43 ± 0.32</td>
</tr>
<tr>
<td>DBA</td>
<td>0.03 ± 0.06</td>
<td>0.18</td>
<td>0.00</td>
<td>0.02 ± 0.01</td>
</tr>
<tr>
<td>BPE</td>
<td>0.17 ± 0.14</td>
<td>0.46</td>
<td>0.04</td>
<td>0.29 ± 0.21</td>
</tr>
<tr>
<td>IPY</td>
<td>0.12 ± 0.15</td>
<td>0.49</td>
<td>0.00</td>
<td>0.35 ± 0.26</td>
</tr>
<tr>
<td>Σ15PAH</td>
<td>2.02 ± 1.50</td>
<td>4.78</td>
<td>0.58</td>
<td>4.17 ± 2.91</td>
</tr>
<tr>
<td>Σ7PAH*</td>
<td>1.08 ± 1.04</td>
<td>3.18</td>
<td>0.21</td>
<td>1.94 ± 1.36</td>
</tr>
</tbody>
</table>


*Carcinogenic PAHs: chrysene, benzo(a)anthracene, benzo(b)fluoranthenes, benzo(k)fluoranthenes, benzo(a)pyrene, indeno(1,2,3-cd) pyrene and dibenz(a)anthracene.
Table 4. Reported total concentrations of PAHs in urban soils (mg·kg⁻¹ dry weight) from a number of studies

<table>
<thead>
<tr>
<th>Location</th>
<th>Study area</th>
<th>Concentrations (mg·kg⁻¹ d.w.)</th>
<th>ΣPAH</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huston, TX, USA</td>
<td>Urban / suburban</td>
<td>0.2-2.2</td>
<td>23</td>
<td>Hwang et al. (2002)</td>
</tr>
<tr>
<td>Mexico City, Mexico</td>
<td>Urban / industrial</td>
<td>0.20-1.10</td>
<td>17</td>
<td>Hwang et al. (2003)</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Urban</td>
<td>0.22-27.82</td>
<td>16</td>
<td>Tang et al. (2005)</td>
</tr>
<tr>
<td>New Orleans, USA</td>
<td>Urban</td>
<td>3.73 (median)</td>
<td>16</td>
<td>Mielke et al. (2001)</td>
</tr>
<tr>
<td>Tarragona County, Catalonia, SP</td>
<td>Urban / residential / industrial</td>
<td>0.11-1.00</td>
<td>16</td>
<td>Nadal et al. (2004)</td>
</tr>
<tr>
<td>Swiss soil monitoring system (NABO), Switzerland</td>
<td>Urban parkland / semiurban</td>
<td>0.05-0.62</td>
<td>16</td>
<td>Bucheli et al. (2004)</td>
</tr>
<tr>
<td>Tallinn, Estonia</td>
<td>Urban</td>
<td>2.20±1.40</td>
<td>12</td>
<td>Trapido (1999)</td>
</tr>
<tr>
<td>Linz, Austria</td>
<td>Industrial</td>
<td>1.45 (median)</td>
<td>18</td>
<td>Weiss et al. (1994)</td>
</tr>
<tr>
<td>Tokushima, Japan</td>
<td>Urban</td>
<td>0.61</td>
<td>13</td>
<td>Yang et al. (2002)</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>Main urban</td>
<td>0.13-8.65 / 0.06-7.22</td>
<td>26 / 16</td>
<td>Wang et al. (2013)</td>
</tr>
<tr>
<td>El-Tabbin, Egypt</td>
<td>Urban / industrial</td>
<td>0.05-5.56</td>
<td>16</td>
<td>Havelevcová et al. (2014)</td>
</tr>
<tr>
<td>Phoenix, Arizona, USA</td>
<td>Urban (highways)</td>
<td>0.06-10.12</td>
<td>20</td>
<td>Manusenko et al. (2010)</td>
</tr>
</tbody>
</table>

Table 5. PAH ratios in studied soils

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Parkland</th>
<th>Residential</th>
<th>Industrial</th>
<th>Indicated source (origin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANT / (ANT + PHE)</td>
<td>0.19</td>
<td>0.09</td>
<td>0.12</td>
<td>Pyrogenic</td>
</tr>
<tr>
<td>FLT / (FLT + PYR)</td>
<td>0.51</td>
<td>0.49</td>
<td>0.50</td>
<td>Gasoline, diesel and crude oil combustion</td>
</tr>
<tr>
<td>BaA / (BaA + CHR)</td>
<td>0.58</td>
<td>0.52</td>
<td>0.51</td>
<td>Grass, coal and wood combustion</td>
</tr>
<tr>
<td>IPY / (IPY + BPE)</td>
<td>0.30</td>
<td>0.40</td>
<td>0.34</td>
<td>Liquid fossil fuel combustion</td>
</tr>
<tr>
<td>BaP / BPE</td>
<td>1.20</td>
<td>1.64</td>
<td>1.31</td>
<td>Traffic sources</td>
</tr>
<tr>
<td>CombPAH / ΣPAH</td>
<td>0.79</td>
<td>0.80</td>
<td>0.81</td>
<td>Combustion dominated source</td>
</tr>
</tbody>
</table>
Table 6. PAH concentrations in urban soils, expressed in BaP eq, mg·kg\(^{-1}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Parkland</th>
<th>Residential</th>
<th>Industrial</th>
<th>TEF(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean × TEF</td>
<td>Max × TEF</td>
<td>Min × TEF</td>
<td>Mean × TEF</td>
</tr>
<tr>
<td>NAP</td>
<td>0.00006</td>
<td>0.00028</td>
<td>0.00003</td>
<td>0.00005</td>
</tr>
<tr>
<td>ANA</td>
<td>0.00002</td>
<td>0.00018</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>FLU</td>
<td>0.00001</td>
<td>0.00023</td>
<td>0.00005</td>
<td>0.00017</td>
</tr>
<tr>
<td>PHE</td>
<td>0.00006</td>
<td>0.00045</td>
<td>0.00005</td>
<td>0.00026</td>
</tr>
<tr>
<td>ANT</td>
<td>0.0006</td>
<td>0.0037</td>
<td>0.0001</td>
<td>0.0004</td>
</tr>
<tr>
<td>FLT</td>
<td>0.00018</td>
<td>0.00035</td>
<td>0.00009</td>
<td>0.00069</td>
</tr>
<tr>
<td>PYR</td>
<td>0.00018</td>
<td>0.00035</td>
<td>0.00009</td>
<td>0.00074</td>
</tr>
<tr>
<td>BaA</td>
<td>0.019</td>
<td>0.053</td>
<td>0.004</td>
<td>0.035</td>
</tr>
<tr>
<td>CHR</td>
<td>0.0015</td>
<td>0.0044</td>
<td>0.001</td>
<td>0.0004</td>
</tr>
<tr>
<td>BbF</td>
<td>0.023</td>
<td>0.069</td>
<td>0.005</td>
<td>0.046</td>
</tr>
<tr>
<td>BKF</td>
<td>0.015</td>
<td>0.0560</td>
<td>0.002</td>
<td>0.019</td>
</tr>
<tr>
<td>BaP</td>
<td>0.22</td>
<td>0.07</td>
<td>0.04</td>
<td>0.43</td>
</tr>
<tr>
<td>DBA</td>
<td>0.15</td>
<td>0.090</td>
<td>0.00</td>
<td>0.10</td>
</tr>
<tr>
<td>BPE</td>
<td>0.0017</td>
<td>0.0046</td>
<td>0.0004</td>
<td>0.0029</td>
</tr>
<tr>
<td>IPY</td>
<td>0.012</td>
<td>0.049</td>
<td>0.00</td>
<td>0.017</td>
</tr>
<tr>
<td>Σ15PAH</td>
<td>0.4435</td>
<td>1.8415</td>
<td>0.0591</td>
<td>0.6553</td>
</tr>
<tr>
<td>Σ7PAH</td>
<td>0.4405</td>
<td>1.8314</td>
<td>0.0511</td>
<td>0.6501</td>
</tr>
</tbody>
</table>

\(^a\)Values of the Toxic equivalency factors proposed by Nisbet and Lagoy (1992).
Fig. 1. Location of the soil sampling sites.

Fig. 2. Structures of the studied PAH compounds.
Fig 3. Distribution pattern of PAHs with different ring numbers in studied soils.

Fig 4. Composition of PAH mixtures in studied soils.
Fig. 5 PAH source apportionment
Fig. 6. LS Means plot, differences of PAH levels in soil between land uses.

Fig. 7. Scale of potential sources of contamination with petroleum products (units per square km) with PHE distribution plots.