



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

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8 **Abstract**

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

32 **1. Introduction**

33 The quantity of toxic organic substances is extremely high, but in the world practice the evaluation of
34 contamination levels of certain areas is produced mostly for polycyclic aromatic hydrocarbons (PAHs), an
35 ubiquitous organic pollutants in environments, particularly in soils and sediments. PAHs are a large group of
36 persistent organic compounds (POPs) consisting of several hundred individual homologues and isomers containing
37 at least two condensed aromatic rings. Their input to the environment has both natural and anthropogenic origins.
38 Natural sources includes releases from vegetation fires, diagenetic processes and volcanic exhalations (ATSDR
39 1995; Wilcke 2000). In turn, anthropogenic PAHs occur from pyrolytic processes, especially incomplete combustion
40 of organic during industrial activities, domestic heating, waste incineration, transportation and power generation
41 (ATSDR 1995; Wilcke 2000; Dyke et al. 2003). It is believed that by far most PAHs are released into environment
42 by anthropogenic combustion of wood and fossil fuels (Wilcke 2000). Sign of anthropogenic contamination of soil
43 with PAHs are even detected in such remote places as Antarctic Stations, which origin is doubted, whether it has
44 natural sources, i.e. decomposition of plant and guano materials, or comes from anthropogenic sources, such as fuel
45 combustion, petroleum products and long range transport with atmospheric solid particles (Abakumov et al. 2014;
46 Abakumov et al. 2015). Some PAHs are of the most environmental importance because of the established
47 carcinogenic, mutagenic and teratogenic effects in living organisms and in humans particularly (Menzie et al. 1992;
48 Shaw and Connell 1994; Perera 1997; Yu 2002; Guo et al. 2013). A number of 16 PAHs have been listed as priority
49 contaminants by both the US Environment Protection Agency (US EPA) and European Union (EU). Among them
50 seven compounds, i.e. benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene,
51 dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene are considered as probable human carcinogens (US EPA 2002).
52 In Canada, US and some European countries normalization of soil contamination is provided upon developed soil
53 quality criteria for selected PAHs or their sum. Only a few countries have established comprehensive soil guideline



54 values (SGV) for particular land use at least for the sum 85 of priority PAHs ($\Sigma 7$; 10; 15; 16). Generally, the
55 existing soil critical values provides only human health-risk based approaches and don't consider protection of other
56 ecological receptors. In turn, US EPA has developed ecological soil screening levels (Eco-SSLs) for PAHs, which
57 are derived separately for four groups of ecological receptors: plants, soil invertebrates, birds and animals. However
58 these screening levels are intended to evaluate an unacceptable ecological risk to terrestrial receptors, they are not
59 designed to be used as cleanup levels. For this purpose US EPA adopted a human health based Preliminary
60 Remediation Goals for Soil (PRG) using estimates of different routes of exposure. In contrast to this, Russian
61 Federation has not yet developed soil guideline values at least for the sum of priority PAHs; normalization is
62 provided only for soil contamination with benzo(a)pyrene without distinction for particular land use. On top of that,
63 no threshold values are provided for other POPs. A summary of soil guideline values for PAHs set in some countries
64 is presented in **supplementary materials 1**. Thus studies on soil contamination with PAHs are of the most
65 importance as they provide information that can be further used to delineate special contaminated sites exhibiting
66 high risk to human exposure. Thousands of reports about PAHs concentrations, sources and health risk assessments
67 in urban and semiurban areas from all over the world were published in recent years. Elevated levels of PAHs in
68 urban soils were reported in Hustan, USA (Hwang et al. 2002), Beijing, China (Tang et al. 2005), Glasgow of UK
69 and Torino of Italy (Morillo et al. 2007), and Esbjerg of Denmark (Essumang et al. 2011).

70 St. Petersburg is the largest industrial and transport center in the northwestern region of Russia and is of
71 great interest from the viewpoint of environmental concern. The ecological status of such a large center reflects the
72 whole range of socioeconomic problems resulting in decline of human health under the influence of various
73 chemical, physical and biological factors. The ecological situation in the city is determined by the emissions from
74 more than a thousand industrial enterprises, large railway junction, seaport and the great motor vehicle fleet – 1 670
75 794 cars and 207 975 trucks as of 2014 (Belousova et al. 2014). All this transport is served by a huge amount of
76 petrol stations and transport companies: currently in St. Petersburg operate 27 fuel operators and 397 petrol stations.
77 Industrial enterprises of the city include high-capacity, resource- and power-consuming ecologically dangerous
78 works. According to the data collected from the automatic air monitoring system of the city in 2014 total emission
79 into the air from both the stationary sources and vehicles has reached 513 200 t in 2014 of chemicals, including 16
80 903 t of hydrocarbons (CH_x), 3000 t of black carbon (BC) and 47 900 t of volatile organic compounds (VOC)
81 (Belousova et al. 2014). The amount of emissions per capita complies 135.9 kg / year, per unit area – 434.5 t / km²
82 (Belousova et al. 2014). At the same time, 91.9% of emissions are accounted to the transport activity. Industrial and
83 transport emissions are the major source of soil contamination with PAHs in urban areas along with inputs from
84 petroleum products. No systematic survey of soil contamination with priority PAHs has been conducted yet in St.
85 Petersburg except for benzo(a)pyrene (Gorkiy and Petrova 2007). Considering this fact and environmental aspects
86 of the territory described above, St. Petersburg affords an excellent location to study geochemical cycles of PAHs.

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

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

95 2. Materials and methods

96 2.1 Study site description

97 Choice of the study area, namely Primorsky, Vasileostrovsky and Kirovsky administrative Districts of St.
98 Petersburg was done in order of increasing of location density of potential stationary sources of contamination with
99 PAHs, population density and traffic activity. Detailed characteristics about each chosen area are given in Table 1.
100 Certain areas of recreational, residential and industrial land use scenarios within each chosen District were subjected
101 under the study. Information on the land use scenario of each chosen area was obtained using online map service
102 “Regional Geoinformational System RGIS” developed with the support of the Committee for land resources and
103 land management of St. Petersburg (Fig. 1). Potential sources of PAH contamination affecting PAH levels in soil
104 here are high traffic activity (Western highway and Primorsky prospect), steel and chemical industries (Kirovsky
105 engineering plant, Baltiysky shipyard plant, varnish factory “Kronos”), thermal-power-stations (“North-Western”).



106 Climate is moderately continental, significantly affected by the Baltic Sea. The average annual amount of
 107 precipitates varies 565-635 mm. Humidity factor – 1.1-1.3. The territory represents an almost flat plain with
 108 altitudes below 20 m above the sea level (Neva Lowland). Natural soil formation usually occurs on ancient lake-
 109 marine littoral sands, sandy loams, loams (less) depleted in calcium (Gagarina et al. 2008). Urban soils are formed
 110 on the bulk deposits ranging from 0.9 to 4 m of thickness (Matinyan et al. 2005; Dashko et al. 2011). Soils are
 111 strongly disturbed by anthropogenic activities (buried, sealed and/or contaminated), with small relatively intact
 112 islands in natural and seminatural areas on the north, north-west and north-east of the City. Soils of the historical
 113 center are presented by anthropogenic soil-like formations called in national soil classification systems as
 114 “urbanozems” (Stroganova e. al. 1992) or “urbiquazizems” (Shishov et al. 2006) and generally characterized by light
 115 grain size, modified soil profiles, with abundant inclusions of anthropogenic artefacts in the form of debris, domestic
 116 wastes and remains of communications, neutral to alkaline pH, high humus, nitrogen and phosphorus content,
 117 humate and fulvic-humate types of humus and traces of chemical contamination (Rusakov et al. 2005; Matinyan et
 118 al. 2005; Ufimtseva et al. 2011). Investigated urban soils were classified as *Technosols* according to the World
 119 Reference Base for soil resources (Michéli et al. 2006).

120 2.2 Sampling strategy and procedure

121 Sampling was conducted in September 2013 at 9 urban sites, in dry and clear weather conditions according
 122 to international standard protocol ISO 10381-1 (2002) and national sampling standard GOST 17.4.4.02-84 (1984).
 123 Soil samples were taken from 0-20 cm topsoil layer. A total of 135 grab soil samples were collected diagonally from
 124 25 m² sampling plots were combined into 27 composite samples of 0.7 kg each one. Location of the sampling sites
 125 was defined according to proximity to residential areas and potential pollution sources (Fig.1).

126 Sampling strategy responds to the study objectives and is aimed to provide comprehensive characterization
 127 of the selected sites suspected to be contaminated with PAHs. Quantity of grab samples to be collected depended on
 128 the size of sampling sites, e.g. 15 grab samples per 0.8 ha site collected from sampling plots ($S = 25 \text{ m}^2$). Soil depth
 129 selected for sampling is a function of exposure routes (e.g. soil ingestion, dermal contact with soil and dust,
 130 inhalation of contaminated dust, inhalation of volatile compounds). Sampling pattern represents both the purposive
 131 and judgement sampling techniques, delineating sample locations that assumed to be representative of the whole site
 132 and most contaminated. Instruments for sample derivation included stainless scoop and stainless knife prewashed
 133 with acetone. The representativeness of collected samples was provided thorough mixing and taking an average
 134 sample by quartering method.

135 **Fig. 1.** Location of the soil sampling sites.

Description to fig. 1			
Land use	a - Primorskij District	b - Vasileostrovskij District	c - Kirovskij District
Parkland	1 - The park of the 300th anniversary of St. Petersburg, Primorskij prospect, 157. 59°59'2" N, 30°11'33" E.	4 - Akademicheskij Garden, 2d Line of Vasilyevskij Island, 2A. 59°56'19.8" N, 30°17'18.3" E. Rumyantsevskij Garden, Rumyantsevskaya square, 7. 59°56'18.4" N, 30°17'33.1" E.	7 - The park of 9th January, Stachek prospect, 19. 59°53'31.1" N, 30°16'25.5" E.
Residential	2 - Intersection of Yahtennaya street and Optikov street. 59°59'55.7" N, 30°13'22.9" E.	5 - Korablestroiteley street, 20, 19/2. 59°56'37.3" N, 30°12'48.3" E. 59°56'38.0" N, 30°13'05.2" E.	8 - Komeev street, 4. 59°53'06.9" N, 30°16'03.8" E.
Industrial	3 - Vicinity of the Bus depot №2, Avtobusnaya street, 12A. 60°01'46.6" N, 30°15'34.7" E.	6 - Vicinity of the Baltic shipyard, Detskaya street, 3. 59°55'36.1" N, 30°15'13.1" E.	9 - Vicinity of the Kirovskij engineering plant, Stachek prospect, 47. 59°53'09.3" N, 30°15'48.1" E.

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

142



143 2.3 HPLC, PAH source identification and risk evaluation

144 15 PAHs were analyzed, including naphthalene (NAP), acenaphthene (ANA), fluorene (FLU),
145 phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene
146 (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(ah)anthracene
147 (DBA), benzo(g,h,i)perylene (BPE), indeno(1,2,3-cd)pyrene (IPY) (**Fig. 2**).

148 **Fig. 2.** Structures of the studied PAH compounds

149 PAHs content in samples were determined on the basis of US EPA method 8310 (1996a), national standard
150 method PND F 16.1:2.2:3.62-09 (2009), and Gabov (2007; 2008). Extraction of the PAHs was carried out at room
151 temperature with methylene chloride (high purity grade) and ultrasonic treatment via Branson 5510 ultrasonic bath
152 (USA, power 469 W, working frequency 42 kHz) following the US EPA method 3550b (1996b). Solvent removal
153 (evaporation) was carried out with Kuderna–Danish concentrator (Supelco). PAHs fractions were purified by
154 consecutive chromatography in columns filled with aluminum oxide (Brockman activity grade 2-3, Neva Reaktiv)
155 and silica gel (Fluka) according to the US EPA purification method 3660c (1996c). The purity was controlled by the
156 absence of peaks in the blank chromatogram. A standard mixture of 15 PAHs (Supelco) with the concentrations of
157 each component in the range of 100–2000 µg/cm³ was used to prepare the standard PAH solutions. Qualitative and
158 quantitative determination of PAHs in soils was carried out by reverse-phase high-performance liquid
159 chromatography (HPLC) in gradient mode with spectrofluorimetric detection via chromatograph "Lyumahrom"
160 ("Lumex", Russia). Chromatography was performed at 30°C on a column Supelcosil™ LC-PAH n5 µm (25 cm ×
161 2.1 mm). Mobile phase was provided with acetonitrile-water gradient. Samples of 10 µl volume were injected using
162 injection valve. Individual PAHs were identified by the time of retention and comparison of fluorescence spectra of
163 the components coming from the column with spectra of the standard PAHs. Quantitative analysis of PAHs was
164 performed by external standard method. For the quality assurance purposes Standard reference materials® 1944
165 New York/New Jersey Waterway Sediment (National Institute of Standards and Technologies NIST, USA)
166 containing a mixture of 15 PAHs were subjected to the procedure described above. The error of measuring the
167 PAHs (benzo[a]pyrene) in the soils was 35% in the range of 5–40 ng/g and 25% in the range of 40–2000 ng/g with a
168 confidence probability of P = 0.95.

169 PAH molecular markers and ratios were used to determine PAH sources (Pandey et al. 1999; Yunker et al.
170 2002; Hwang et al. 2003). Sum of combustion PAHs (CombPAH/15PAH) was used as tracer of pyrogenic sources.
171 CombPAH/15PAH marker indicates portion of the sum of combustion specific compounds in total PAH content,
172 which are Fluoranthene, Pyrene, Chrysene, Benzo(a)anthracene, Benzo(k)fluoranthene, Benzo(b)fluoranthene,
173 Benzo(a)pyrene, Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene (Prahel and Carpenter, 1983). Applied PAH
174 molecular markers and ratios as well as their ranges are given in **supplementary materials 2**.

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

181 2.4 Soil properties analysis and statistical treatment

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

188 Measured TOC concentrations in studied samples ranged between 3.82 to 6.41% with a median value of
189 4.80%. Numerous studies suggested that soil organic matter (SOM) content plays an important role in retention of
190 PAH in soil (Conte et al. 2001; Chung and Alexander 2002). In simple terms the higher SOM concentrations are,
191 than the higher amount of PAHs can be absorbed (Karickhoff and Brown, 1979; Wilcke, 2000). Entering the soil
192 from the atmosphere PAHs are preferentially sorbed to aggregate surfaces (Wilcke, 1996). The close association of
193 PAHs with SOM results in differentiation of organic contaminants pools among particle-size fractions
194 (Guggenberger et al. 1996). A significant increase of PAH concentrations in finer fractions is shown in a number of



195 studies (Wilcke, 1996). Clay content in studied soils ranges between 1.87 and 8.50 %. A correlation coefficients
196 were calculated in present study in order to reveal relationship between levels of PAH in soil and analyzed soil
197 parameters. A strong positive correlation was found between sum of 15 PAH in soil and clay content ($r = 0.91$; $n =$
198 27 ; $p = 0.95$), however, no correlation of total PAH and TOC concentrations in soil was detected.

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

211 3. Results and discussion

212 3.1 PAH concentrations in studied soils

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

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

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

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

237 The pie chart illustrating composition of PAH mixtures in soils is depicted in **Fig. 4**. The obvious equality
238 in PAH distribution patterns in all studied sites clearly indicates the common source of PAHs. Pyrene and
239 Fluoranthene (4-ring PAHs) are the most abundant compounds in examined samples, portion of which accounts for
240 16-18 % of 15PAH. The following predominant compounds are 5-ring PAH benzo(b)fluoranthene (10-11%) and
241 benzo(a)pyrene (8-11%). The rest portion of the sum is represented by lighter weight PAHs (2-3-ring PAHs) and is
242 generally dominated by Phenanthrene (6-9%). Domination of 4 and 5-ring PAHs, mainly PYR, FLT, BbF and BaP,
243 in studied soils is indicative of elevated diesel fuel consumption activity on the territory. Estimated diesel
244 consumption in St. Petersburg reaches 38% of the total fuel use for transportation (Belousova et al. 2014). As known
245 emission rate of heavyweight PAH fraction due to diesel combustion is several times higher (Sjogren et al. 1996;
246 Marr et al. 1999).



247 **Fig 4.** Composition of PAH mixtures in studied soils

248 Obtained data are nearly consistent with data from Lodygin et al. (2008) exploring PAH levels (sum of 11
249 PAHs) in soils of Vasilievsky Island in St. Petersburg). The main anthropogenic impact on soils of residential area
250 of the island was exerted by light polyarens, including 2-4 ring substances (as stated by the author), the portion of
251 which in the total content of PAHs was more than 50%. Maximum concentrations of PAHs were detected in soils
252 along highways with intense traffic and considerable emission of combustion gases. The reported total PAH content
253 ranged from 0.197 to 8.20 mg·kg⁻¹ between different land utilization types. The described distribution patterns of
254 individual PAHs are similar to those of this study: the most abundant are 4-5 ring PAHs, particularly Pyrene (17%),
255 Fluoranthene (17%), Benzo(g,h,i)perylene (13%), Benzo(b)fluoranthene (12%) and Benzo(a)pyrene (12%). Several
256 samples were noticed to exhibit higher contents of heavy polyarens of natural origin, as both of the samples were
257 represented by fresh organic material (peat) which is used as amendment in soils of residential areas and roadsides.
258 Thus the findings of above mentioned study suggest that spatial distribution of PAHs is mainly dictated by the
259 closeness to highways and by the artificial input of peat material in the urban soils.

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

266 Total PAH concentrations in soils of urban and industrial sites from a number of investigations set in other
267 countries are summarized in **Table 4**. Tang et al. (2005) reported a sum of 16 PAHs of 27.82 mg·kg⁻¹ in roadside
268 soils of Beijing, China. Hwang et al. (2002) found a total PAH concentration of 0.20-2.20 mg·kg⁻¹ in urban and
269 suburban soils in Huston, Texas, USA. Notable PAH concentrations were observed by Mielke et al. (2001) in New
270 Orleans urban soils (USA), fluctuating around a medium level of 3.73 mg·kg⁻¹. Nadal et al. (2004) reported
271 relatively lower 16 PAHs levels in soils of the vicinity of the chemical and petrochemical industries and
272 urban/residential sites in Tarragona County (Catalonia, Spain), ranging **284** between 0.11 and 1.0 mg·kg⁻¹.
273 Comparable findings were announced by Bucheli et al. (2004) for soils of urban and semiurban areas in Switzerland,
274 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,
275 which is mainly attributed with influence of the anthropogenic activities on the studied territories.

276 **3.2 Determination of the PAH sources and statistics**

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

286 **Fig. 5** PAH source apportionment

287 Several markers are indicative of certain combustion sources of PAHs, appointing to gasoline, diesel, crude
288 oil or grass, coal and wood combustion origins, namely: FLT/(FLT+PYR), BaA/(BaA+CHR), IPY/(IPY+BPE) and
289 BaP/BPE. The calculated FLT/(FLT+PYR) (0.49-0.51), IPY/(IPY+BPE) (0.30-40) and BaP/BPE (1.20-1.64) values
290 point to a domination of gasoline, diesel and oil combustion. However, obtained values of FLT/(FLT+PYR) and
291 BaA/(BaA+CHR) ratios suggested that coal and wood combustion have a certain role in PAHs origination as well. It
292 is important to note that the shift of heavy and low molecular PAHs ratio towards the heavy ones cannot be
293 explained only by anthropogenic factor, the degradation of lighter PAHs due to environmental factors such as
294 photolysis under the direct sun rays in the topsoil layers, as well as thermal degradation, biological uptake and
295 biodegradation may play a significant role as well (Behymer and Hites 1985; Wild and Jones 1995; Wang 1998;
296 Johnsen 2005; Choi et al. 2010). These processes are predetermined by physical and chemical properties of the
297 lighter fraction PAHs such as low molecular weight, high vapor pressure and high volatility rate (Mackay and
298 Hickie 2000). Volatilization was proved to play the most significant role in the global degradation of the 2- and 3-



299 ringed PAHs especially. Park et al. (1990) reported that approximately 30% loss of Naphthalene accounts for
300 volatilization, while for the remaining compounds this process was insignificant. Heavy weight PAHs, i.e. 4-6-ring
301 compounds, have low solubility in water and low volatility, strong affinity to particulates (BC and SOM, fine
302 fractions), are less accessible for biological uptake and degradation and thus are more persistent in the environment
303 (Johnsen 2005; Haritash 2009). It has been proven that PAHs may form nonextractable [¹⁴C]PAH residues in soil
304 under the stimulation of microbial activity, which obviously leads to unexpected lower results while analyzing the
305 concentrations of Naphthalene, Anthracene, Pyrene and Benzo(a)pyrene in soil samples (Eschenbach et al. 1994;
306 Eschenbach et al. 1998).

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

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

310 The differences in levels of individual PAH compounds were tested using Post-hoc Fisher LSD test. The
311 results showed significant differences of FLT, PYR and PHE concentrations between parkland, residential and
312 industrial areas ($p = 0.01-0.03$). The tested hypothesis suggested that PAH levels in urban soil may differ between
313 areas with different land utilization type, following the order: industrial, residential, parkland. Thus the results of the
314 study did not prove the tested hypothesis, suggesting the argument of equal PAHs load on the urban soils. The land
315 use factor is expressed only in distribution of the dominant individual PAHs, particularly FLT and PYR. These
316 compounds are known to be a part of the PAHs mixtures isolated from the exhaust gases and industrial emissions
317 (Fernandes et al. 1997; Rehwagen et al. 2005). So not too surprising, that elevated levels of these pollutants are
318 expected primarily in industrial and transport areas along with surroundings, where maximum input of black carbon
319 from air pollution sources is noted. PHE representing low molecular weight PAH is a thermodynamically stable tri-
320 aromatic compound arising from petroleum-hydrocarbon-based releases. Distribution of this contaminant follows
321 the scheme of potential sources of contamination with petroleum products allocation (**Fig 7**).

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

324 3.3 Risk evaluation of PAHs in soils

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

328 The calculated BaP_{eq} on the average concentration of 15PAH (here and after referred to BaP_{eq}-15PAH)
329 varied between 0.44 to 0.66 mg·kg⁻¹ dry soil. The highest BaP_{eq}-15PAH mean concentrations were found in
330 residential and industrial areas – 0.66 and 0.55 mg·kg⁻¹ respectively. Parkland areas are characterized by the lower
331 but still considerable levels of BaP_{eq}-15PAH (mean 0.44 mg·kg⁻¹). It is to be noted that one single sample taken
332 from the Kirovskij parkland exhibited a total BaP_{eq} concentration of 1.84 mg·kg⁻¹ (The park of 9th January), which
333 evidently shows that parkland land uses are subjected under a high load of PAHs as well as other land uses.
334 Obtained values are several times higher than reported total PAHs carcinogenic potencies in a number of studies
335 (BaP_{eq} of total PAHs): 0.02 mg·kg⁻¹ in soils of Viseu and 0.23 mg·kg⁻¹ in Lisbon, Portugal (Cachada et al. 2012);
336 Nadal et al. (2004) reported BaP_{eq} concentrations varying between 0.02 to 0.12 mg·kg⁻¹ in soils of Tarragona
337 County, Spain; 0.18 mg·kg⁻¹ in soils of Beijing and 0.24 mg·kg⁻¹ in Shanghai, China (Liu et al. 2010; Wang et al.
338 2013).

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

345 4. Conclusions

346 Results of the study demonstrated that soils within urban areas with different land utilization types are
347 characterized by common loads of PAHs generally attributed to high traffic density of the city. Considerable levels
348 of soil contamination with PAHs were noted. The common tendency in PAH distribution patterns between
349 investigated sites clearly indicates the common source of PAHs in urban soils. A larger portion of high molecular
350 weight PAHs along with determined molecular ratios suggest the predominance of pyrogenic sources, mainly



351 attributed to combustion of gasoline, diesel and oil. Petrogenic sources of PAHs have a significant portion as well
352 defining the predominance of petroleum associated low molecular weight PAHs such as phenanthrene. Derived
353 concentrations of 7 carcinogenic PAHs as well as calculated BaP total potency equivalents were multiple times
354 higher than reported in a number of other studies, indicating a significant risk for human health in case of direct
355 contact. One-way ANOVA results showed significant differences in levels of pyrene, fluoranthene and
356 phenanthrene – the most abundant individual PAHs in examined sampled, between parkland, residential and
357 industrial land uses, suggesting the influence of land use factor on distribution of these pollutants. Further study with
358 an application of complex statistical methods is needed such as principal component analysis which would
359 contribute to precision of PAHs sources allocation.

360 Acknowledgments

361 This work was supported by Russian Foundation for Basic Research, project № [15-34-20844](#)

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555

556 **Table 1.** Description of the study area

Characteristics	Units	Primorsky District	Vasileostrovsky District	Kirovsky District
S	km ²	109.87	17.1	47.10
Population	-	534 646	211 048	334746
Industries	units	250	350	70
Number of potential contamination sources with petroleum products	units	14	7	10
Density of potential contamination sources	units per km ²	0.13	0.41	0.21
CH _x emissions from stationary sources in 2014	thousand tons	0.556	0.034	0.708
VOC emissions from stationary sources in 2014	thousand tons	0.153	0.099	0.545
BC emissions from stationary sources in 2014	thousand tons	0.237	0.037	0.174

557 **Table 2.** Physicochemical properties of the studied soils

District	Land use	Soil type. FAO	TOC	Clay
			%	
Primorskiy	Parkland	Mollic Technosol	4.10 ± 0.01	5.83 ± 0.21
	Residential	Urbic Technosol	3.82 ± 0.03	7.43 ± 0.06
	Industrial	Urbic Technosol	5.49 ± 0.02	8.50 ± 0.10
Vasileostrovskiy	Parkland	Mollic Technosol	5.39 ± 0.01	7.3 ± 0.20
	Residential	Urbic Technosol	6.41 ± 0.02	1.87 ± 0.12
	Industrial	Urbic Technosol	5.28 ± 0.02	3.27 ± 0.15
Kirovskiy	Parkland	Mollic Technosol	4.19 ± 0.03	7.5 ± 0.10
	Residential	Urbic Technosol	4.80 ± 0.03	3.27 ± 0.15
	Industrial	Urbic Technosol	3.09 ± 0.02	7.67 ± 0.06


Table 3. PAH mean concentrations in soils of St. Petersburg (mg·kg⁻¹).

Compound	Parkland (n = 9)			Residential (n = 9)			Industrial (n = 9)			P One-way ANOVA (α = 0.05)
	Mean ± SD	Max	Min	Mean ± SD	Max	Min	Mean ± SD	Max	Min	
	NAP	0.06 ± 0.08	0.28	0.03	0.05 ± 0.02	0.07	0.00	0.09 ± 0.07	0.21	
ANA	0.02 ± 0.06	0.18	0.00	0.00	0.01	0.00	0.00	0.03	0.00	0.41
FLU	0.10 ± 0.06	0.23	0.05	0.17 ± 0.11	0.40	0.03	0.17 ± 0.11	0.31	0.06	0.28
PHE	0.16 ± 0.13	0.45	0.05	0.26 ± 0.17	0.47	0.03	0.36 ± 0.22	0.65	0.07	0.10
ANT	0.06 ± 0.11	0.37	0.01	0.04 ± 0.04	0.11	0.00	0.05 ± 0.03	0.09	0.01	0.87
FLT	0.18 ± 0.07	0.35	0.09	0.69 ± 0.52	1.49	0.04	0.72 ± 0.48	1.50	0.11	0.02
PYR	0.18 ± 0.08	0.35	0.09	0.74 ± 0.55	1.67	0.04	0.70 ± 0.46	1.50	0.16	0.02
BaA	0.19 ± 0.17	0.53	0.04	0.35 ± 0.26	0.64	0.02	0.30 ± 0.20	0.67	0.07	0.32
CHR	0.15 ± 0.14	0.44	0.01	0.31 ± 0.24	0.69	0.02	0.28 ± 0.18	0.54	0.07	0.24
BbF	0.23 ± 0.21	0.69	0.05	0.46 ± 0.30	0.84	0.02	0.41 ± 0.30	1.00	0.10	0.21
BkF	0.15 ± 0.17	0.56	0.02	0.19 ± 0.14	0.36	0.01	0.16 ± 0.11	0.33	0.04	0.82
BaP	0.22 ± 0.22	0.70	0.04	0.43 ± 0.32	0.87	0.02	0.34 ± 0.23	0.73	0.07	0.30
DBA	0.03 ± 0.06	0.18	0.00	0.02 ± 0.01	0.04	0.00	0.02 ± 0.03	0.08	0.00	0.93
BPE	0.17 ± 0.14	0.46	0.04	0.29 ± 0.21	0.52	0.01	0.27 ± 0.20	0.69	0.06	0.39
IPY	0.12 ± 0.15	0.49	0.00	0.17 ± 0.17	0.45	0.01	0.15 ± 0.13	0.38	0.00	0.76
∑ 15PAH	2.02 ± 1.50	4.78	0.58	4.17 ± 2.91	8.10	0.33	4.02 ± 2.61	8.06	0.86	0.16
∑ 7PAH ^a	1.08 ± 1.04	3.18	0.21	1.94 ± 1.36	3.47	0.10	1.66 ± 1.13	3.20	0.36	0.35

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

^a Carcinogenic PAHs: chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd) pyrene and dibenz(a,h)anthracene.

**Table 4.** Reported total concentrations of PAHs in urban soils ($\text{mg}\cdot\text{kg}^{-1}$ dry weight) from a number of studies

Location	Study area	Concentrations ($\text{mg}\cdot\text{kg}^{-1}$ d.w.)	ΣPAH	Reference
Huston, TX, USA	Urban / suburban	0.2-2.2	23	Hwang et al. (2002)
Mexico City, Mexico	Urban / industrial	0.20-1.10	17	Hwang et al. (2003)
Beijing, China	Urban	0.22-27.82	16	Tang et al. (2005)
New Orleans, USA	Urban	3.73 (median)	16	Mielke et al. (2001)
Tarragona County, Catalonia, Spain	Urban / residential / industrial	0.11-1.00	16	Nadal et al. (2004)
Swiss soil monitoring system (NABO), Switzerland	Urban parkland / semiurban	0.05-0.62	16	Bucheli et al. (2004)
Tallinn, Estonia	Urban	2.20±1.40	12	Trapido (1999)
Linz, Austria	Industrial	1.45 (median)	18	Weiss et al. (1994)
Tokushima, Japan	Urban	0.61	13	Yang et al. (2002)
Shanghai, China	Main urban	0.13-8.65 / 0.08-7.22	26 / 16	Wang et al. (2013)
El-Tabbin, Egypt	Urban / industrial	0.05-5.56	16	Havelcová et al. (2014)
Phoenix, Arizona, USA	Urban (highways)	0.06-10.12	20	Marusenko et al. (2010)

Table 5. PAH ratios in studied soils

Ratio	Parkland	Indicated source (origin)	Residential	Indicated source (origin)	Industrial	Indicated source (origin)
ANT / (ANT + PHE)	0.19	Pyrogenic	0.09	Petrogenic	0.12	Pyrogenic
FLT / (FLT + PYR)	0.51	Grass. coal and wood combustion	0.49	Gasoline. diesel and crude oil combustion	0.50	Gasoline. diesel and crude oil combustion
BaA / (BaA + CHR)	0.58	Grass. coal and wood combustion	0.52	Grass. coal and wood combustion	0.51	Grass. coal and wood combustion
IPY / (IPY + BPE)	0.30	Liquid fossil fuel combustion	0.40	Liquid fossil fuel combustion	0.34	Liquid fossil fuel combustion
BaP / BPE	1.20	Traffic sources	1.64	Traffic sources	1.31	Traffic sources
CombPAH / ΣPAH	0.79	Combustion dominated source	0.80	Combustion dominated source	0.81	Combustion dominated source

**Table 6.** PAH concentrations in urban soils, expressed in BaP_{eq} , $\text{mg}\cdot\text{kg}^{-1}$

Compound	Parkland			Residential			Industrial			TEF ^a
	Mean × TEF	Max × TEF	Min × TEF	Mean × TEF	Max × TEF	Min × TEF	Mean × TEF	Max × TEF	Min × TEF	
NAP	0.00006	0.00028	0.00003	0.00005	0.00007	0.00	0.00009	0.00021	0.00	0.001
ANA	0.00002	0.00018	0.00	0.00	0.00001	0.00	0.00	0.00003	0.00	0.001
FLU	0.0001	0.00023	0.00005	0.00017	0.0004	0.00003	0.00017	0.00031	0.00006	0.001
PHE	0.00016	0.00045	0.00005	0.00026	0.00047	0.00003	0.00036	0.00065	0.00007	0.001
ANT	0.0006	0.0037	0.0001	0.0004	0.0011	0.00	0.0005	0.0009	0.0001	0.01
FLT	0.00018	0.00035	0.00009	0.00069	0.00149	0.00004	0.00072	0.0015	0.00011	0.001
PYR	0.00018	0.00035	0.00009	0.00074	0.00167	0.00004	0.0007	0.0015	0.00016	0.001
BaA	0.019	0.053	0.004	0.035	0.064	0.002	0.03	0.067	0.007	0.10
CHR	0.0015	0.0044	0.0001	0.0031	0.0069	0.0002	0.0028	0.0054	0.0007	0.01
BbF	0.023	0.069	0.005	0.046	0.084	0.002	0.041	0.10	0.01	0.10
BkF	0.015	0.0560	0.002	0.019	0.036	0.001	0.016	0.033	0.004	0.10
BaP	0.22	0.7	0.04	0.43	0.87	0.02	0.34	0.73	0.07	1.00
DBA	0.15	0.90	0.00	0.10	0.20	0.00	0.10	0.40	0.00	5.00
BPE	0.0017	0.0046	0.0004	0.0029	0.0052	0.0001	0.0027	0.0069	0.0006	0.01
IPY	0.012	0.049	0.00	0.017	0.045	0.001	0.015	0.038	0.00	0.10
Σ15PAH	0.4435	1.84154	0.05191	0.65531	1.31631	0.02644	0.55004	1.3854	0.0928	
Σ7PAH ^a	0.4405	1.8314	0.0511	0.6501	1.3059	0.0262	0.5448	1.3734	0.0917	

^a Values of the Toxic equivalency factors proposed by Nisbet and Lagoy (1992).

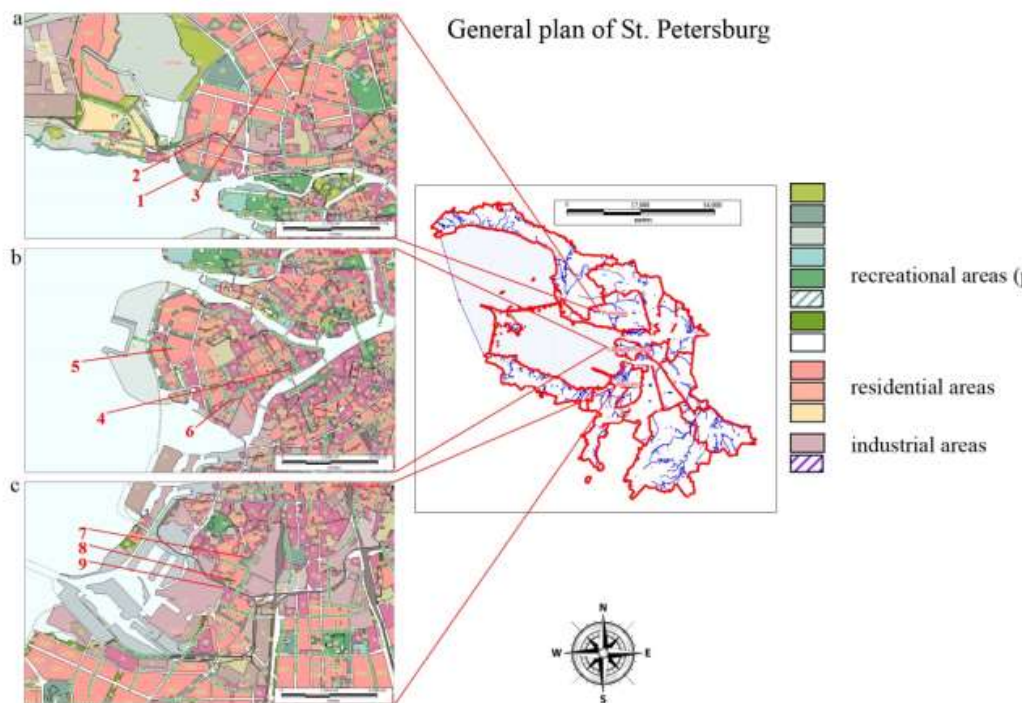


Fig. 1. Location of the soil sampling sites.

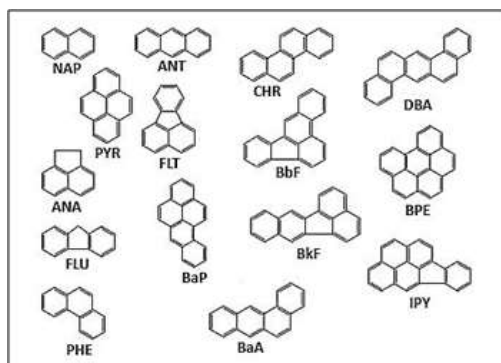


Fig. 2. Structures of the studied PAH compounds.

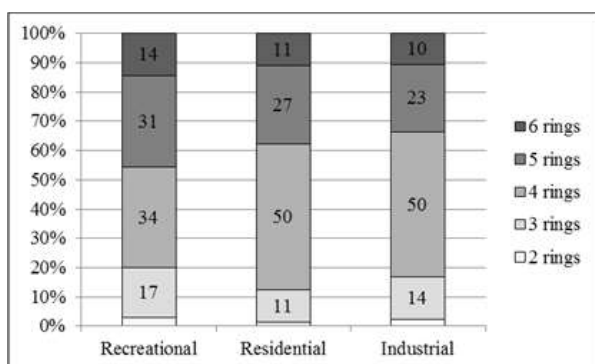


Fig 3. Distribution pattern of PAHs with different ring numbers in studied soils

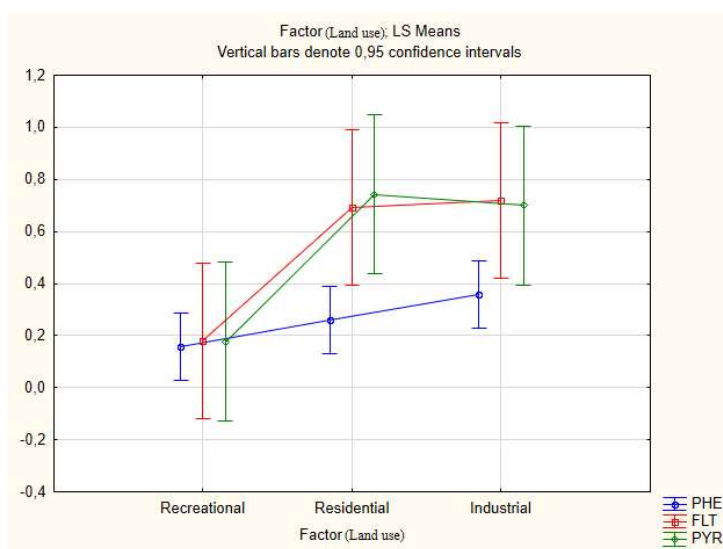


Fig 4. Composition of PAH mixtures in studied soils

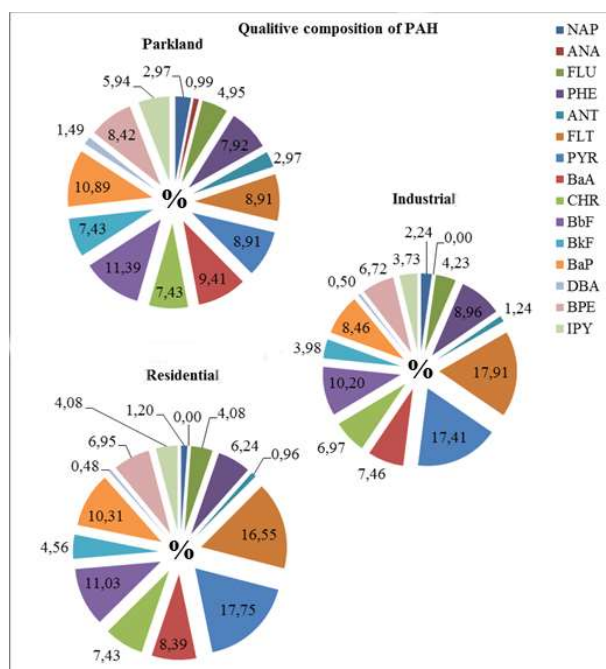


Fig. 5 PAH source apportionment

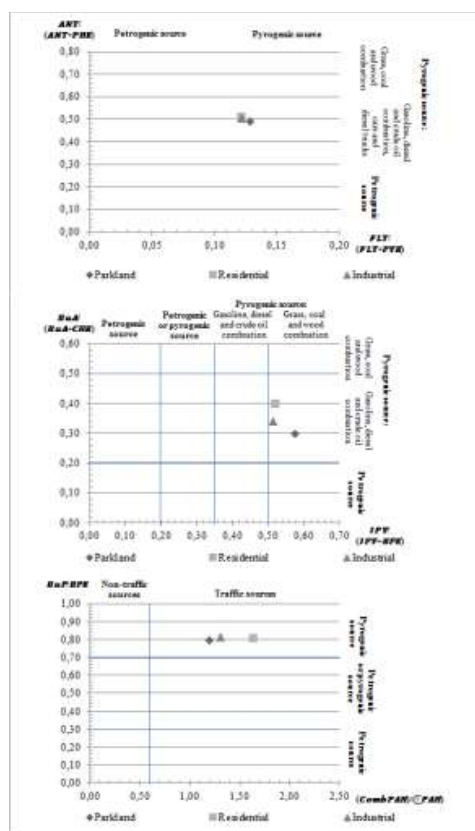


Fig. 6. LS Means plot, differences of PAH levels in soil between land uses

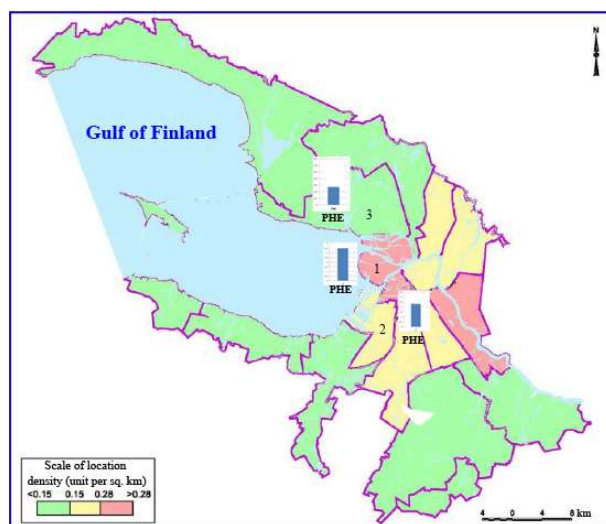


Fig. 7. Scale of potential sources of contamination with petroleum products (units per square km) with PHE distribution plots