Polycyclic aromatic hydrocarbons 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. Benzo(a)pyrene toxic equivalency factors (TEFs) were used to calculate BaP_{eq} in order to evaluate carcinogenic risk of soil contamination with PAHs. Results of the study demonstrated that soils within residential and industrial areas 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}. 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_{eq} were multiple times higher than reported in a number of other studies. The obtained BaP_{eq} 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). However, estimated incremental life time risks posed to population through distinct routes of exposure were under acceptable range. One-way ANOVA results showed significant differences in total PAHs and the sum of 7 carcinogenic PAH concentrations as well as in levels of FLU, PHE, FLT, PYR, BaA, CHR, BbF, BaP and BPE between parkland, residential and industrial land uses, suggesting the influence of land use factor.

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 (Wilcke 2000). PAHs are a large group of aromatic organic compounds 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; Wilcke 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; Wilcke 2000). It is believed that by far most PAHs are released into environment by anthropogenic combustion of wood and fossil fuels (Wilcke 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 (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 semiurban areas from all over the world were published in recent years (Yunker et al. 2002; Liu et al. 2010; Wand et al. 2013). 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 / km^2 (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 load 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 Primorskiy, Vasileostrovskiy and Kirovskiy administrative Districts of St. Petersbrg 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 Primorskiy prospect), steel and chemical industries (Kirovskiy 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 (Gagarina 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. An example of natural soils in St. Petersburg are Albeluvisols, which are wide spread in suburb territories of the Leningradsky region. Soils of the historical center are presented by anthropogenic soil-like formations called in national soil classification systems as "*urbanozems*" (Stroganova e. al. 1992) or "*urbiquazizems*" (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 tothe World Reference Base for soil resources (Michéli 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 см topsoil layer. A total of 135 grab soil samples were collected diagonally from 25 m^2 sampling plots. Single samples 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 a, b, c).

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 sampling sites ranged between 2 to 5 per each zone. The description of sampling sites providing information on location, proximity to potential sources of contamination, population density, road traffics and dominating wind direction is given in supplementary materials 3. All the sampling plots were located near highways with different traffic rates with a distance of no far then 200 meters. Distance between sampling plots ranged between 100 and 200 meters. Total quantity of sampling plots was 34. The sampling depth was common between all sites and matched to a topsoil layer of 0-20 cm. Depth of 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). 5 single initial samples of 0.05 kg each one collected diagonally from 25 m^2 sampling plots were combined into one grab sample of 0.1-0.2 kg, packed in dark glass flask, marked, transported to laboratory and stored at +4° C. A total of 135 grab soil samples were collected. Grab samples were combined into 27 composite samples of 0.7 kg each one. Sampling scheme represents both the purposive and judgment 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 (a). Location of the sampling sites.

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 0.25mm caprone sieve and finally stored in the dark glass containers prewashed with acetone until analysis. This method allows 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(ah)anthracene(DBA), benzo(g,h,i)perylene (BPE), indeno(1,2,3-cd)pyrene (IPY).

PAHs content in samples were determined on the basis of US EPA method 8310 (1996a),national standard method PND F 16.1:2:2.2:3.62-09 (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 5510 ultrasonic bath (USA, power 469 W, working frequency 42 kHz)following the US EPA method 3550b (1996b). 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 Reaktiv) and silica gel (Fluka) according to the USEPA purification method 3660c (1996c). 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 μg/cm^{3}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 "Lyumahrom" ("Lumex", Russia). Chromatography was performed at 30°C on a column Supelcosil ™ 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 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 35% in the range of 5–40 ng/g and25% 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 (Yunker et al. 2002; Hwang et al. 2003, Wang et. Al 2015; Wang et. al. 2017). 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 Fluoranthene, Pyrene, Chrysene, Benzo(a)anthracene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, Benzo(a)pyrene, Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene (Prahl and 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 it to 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.

Site-specific ILCR was calculated in derived soil samples taken from areas with different land uses by application of the Risk Exposure model for chemicals of the Risk Assessment Information System (RAIS). This calculation estimates a theoretical excess cancer risk expressed as the proportion of a population that may be affected by a carcinogen during a lifetime of exposure. The cancer risks (CRs) via ingestion, dermal contact and inhalation of soil particles as well a total cancer risks were estimated using the following Eqs. (1) and (2) and (3), respectively (USEPA, 2004):

$$CR_{ing} = \frac{C_{soil} \times IR_{soil} \times EF \times ED \times CF}{BW \times AT} \times CSF_0, \qquad (1)$$

where CR_{ing} is the cancer risk (unitless) through ingestion of soil particles. C_{soil} is the total BaP$_{eq}$ concentrations of soil PAHs; IR_{soil} is the soil ingestion rate (mg·d^{-1}); EF is the exposure frequency (d·year^{-1}), ED is the exposure duration (years); CF is conversion factor of 10^{-6} mg·kg^{-1} ; BW is body weight (kg), AT is the average life span (d), CSF_o is oral (ingestion) cancer slope factor ((mg·kg^{-1}·d^{-1})$^{-1}$), CSF_o = 7.3 (mg·kg^{-1}·d^{-1})$^{-1}$, for BaP (USEPA, 2013).

$$CR_{derm} = \frac{C_{soil} \times SA \times AF_{soil} \times ABS \times EF \times ED \times CF}{BW \times AT} \times \frac{CSF_0}{GIABS}, \qquad (2)$$

193 where CR_{derm} is the cancer risk (unitless) for dermal contact pathway; SA is the exposed surface area of the skin
194 (cm^2), AF_{soil} is the dermal adherence factor (mg·cm^{-2}), ABS is absorption factor (unitless); and $GIABS$ is fraction of
195 contaminant absorbed in gastrointestinal tract (unitless).

$$CR_{inh} = \frac{C_{soil} \times IR_{air} \times EF \times ED}{PEF \times BW \times AT} \times CSF_i \qquad (3)$$

196 where CR_{inh} is the cancer risk (unitless) for inhalation pathway. IR_{air} is the inhalation rate (m^3·d^{-1}), CSF_i is inhalation
197 cancer slope factor ((mg·kg^{-1}·d^{-1})$^{-1}$), CSF_i is obtained from inhalation unit risk (IUR, (μg·m^{-3})$^{-1}$) of BaP according to
198 the recommended method by USEPA (2013). PEF is the soil particle emission factor (m^3·kg^{-1}). The total lifetime
199 carcinogenic risk ($TLCR$) was calculated by summing the CRs of the 2 age groups.

2.4 Soil properties analysis and statistical treatment

201 Total organic carbon (TOC) was determined using a "Leco" CHN-628 elemental analyzer (USA,
202 combustion temperature 1030 °C, oxygen boost time 28 s). Inorganic carbonates were removed before analysis by
203 acidification in situ of the grounded samples with 1 M hydrochloric acid in order to avoid uncertainty in TOC
204 determination. Clay content was determined with laser diffractometer "Shimadzu" SALD-2201 (Japan). All
205 measurements were done in triplicate. All measurements were converted to absolutely dry sample.

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

3. Results and discussion

3.1 Soil properties and PAH concentrations in studied soils

220 Data on analyzed properties of the studied soils is presented in **Table 2**. Measured TOC concentrations in
221 studied samples ranged between 3.82 to 6.41% with a median value of 4,80%. Numerous studies suggested that soil
222 organic matter (SOM) content plays an important role in retention of PAH in soil (Chung and Alexander 2002). In
223 simple terms the higher SOM concentrations are, than the higher amount of PAHs can be absorbed (Wilcke, 2000).
224 Entering the soil from the atmosphere PAHs are preferentially sorbed to aggregate surfaces (Wilcke, 1996). The
225 close association of PAHs with SOM results in differentiation of organic contaminants pools among particle-size
226 fractions (Guggenberger et al. 1996). A significant increase of PAH concentrations in finer fractions is shown in a
227 number of studies (Wilcke, 1996). Clay content in studied soils ranges between 1.87 and 8.50 %. A correlation
228 coefficients were calculated in present study in order to reveal relationship between levels of PAH in soil and
229 analyzed soil parameters. A strong positive correlation was found between sum of 15 PAH in soil and clay content (r
230 = 0.91; n = 27; p = 0.95), however, no correlation of total PAH and TOC concentrations in soil was detected.

231 The levels of 15 individual PAH compounds analyzed in soils are shown in **Table 3**. The sum of 15 PAH
232 and the sum of 7 compounds included in the group of probable human carcinogens (B2) by the US EPA (1993) are
233 given additionally. Total PAH concentrations in studied soils were found to range from traces to 8.06 mg·kg^{-1} (sum
234 of 15 priority PAH, hereafter referred to 15PAH). The vast majority of samples were characterized by
235 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
236 countries. The highest 15PAH levels were observed in soil samples collected from residential and industrial sites
237 reaching an average of 4.17 and 4.02 mg·kg^{-1} respectively with a maximal value of 8.06 mg·kg^{-1} for industrial site in
238 Kirovskiy district (hereafter – K.D.) Concentrations found in parkland areas were substantially lower than those of
239 residential and industrial, with an average value of 1.08 mg·kg^{-1}.

240 Distribution of the sum of the 7 carcinogenic PAH (7PAH) in soils of the studied urban sites is generally
241 characterized by the same pattern as the total PAH content in soils. The highest 7PAH levels were measured in soil
242 samples taken from residential sites (1.94mg·kg^{-1}) with an absolute value of 3.47 mg·kg^{-1} in technosol of K.D.

243 residential area. 7PAH levels in parkland areas tend to be at lower range respectively to distribution of 15PAH. All
244 sampling sites were located in a proximity of less than 250 m to the highways (Korablestroiteley street, Stachek
245 prospect, Optikov prospect, University embankment, Bolshoi prospect V.O. and others) showing heavy traffic. The
246 portion of 7PAH to the 15PAH in all tested samples ranged between 41 % and 46 %, which evidently shows that the
247 soils may represent considerable health risk for human.

248   The sum of organic pollutants is mostly dominated by heavy molecular weight PAH with 4-5 rings. Portion
249 of 4-ringed PAH compounds in soil of residential and industrial sites accounts for 50% of the sum decreasing to
250 34% in parkland soils. 5-ringed PAH including such compounds as BaP, BbF, BkF, and DBA contribute up to 31 %
251 of the sum of PAH insignificantly varying between studied areas. The rest portion is accounted for the 6-ringed (10-
252 14%) and low molecular weight PAHs with 2 or 3 rings in structure (11-17%).

253   The pie chart illustrating composition of PAH mixtures in soils is depicted in **Fig. 2.** The obvious equality
254 in PAH distribution patterns in all studied sites clearly indicates the common source of PAHs. Pyrene and
255 Fluoranthene (4-ring PAHs) are the most abundant compounds in examined samples, portion of which accounts for
256 16-18 % of 15PAH. The following predominant compounds are 5-ring PAH benzo(b)fluoranthene (10-11%) and
257 benzo(a)pyrene (8-11%). The rest portion of the sum is represented by lighter weight PAHs (2-3-ring PAHs) and is
258 generally dominated by Phenanthrene (6-9%). Domination of 4 and 5-ring PAHs, mainly PYR, FLT, BbF and BaP,
259 in studied soils is indicative of elevated diesel fuel consumption activity on the territory. Estimated diesel
260 consumption in St. Petersburg reaches 38% of the total fuel use for transportation (Belousova et al. 2014). As known
261 emission rate of heavyweight PAH fraction due to diesel combustion is several times higher (Marr et al. 1999).

262 **Fig 2.** Composition of PAH mixtures in studied soils

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

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

281   Total PAH concentrations in soils of urban and industrial sites from a number of investigations set in other
282 countries are summarized in **Table 4.** In general terms, the predominance of 3-5 ring PAHs is noted, which is
283 mainly attributed with influence of the anthropogenic activities on the studied territories.

284   **3.2 Determination of the PAH sources**

285   While a domination of high molecular weight PAH fraction indicates a combustion origin (pyrogenic),
286 enrichment of low molecular weight PAHs is common in fresh fuels (petrogenic) (Budzinski et. al. 1997). Special
287 molecular markers and ratios, proposed by Yunker et al. (2002) and a total combustion PAHs index, reported by
288 Hwang et al. (2003) were applied for PAH sources apportionment. Obtained meanings of applied PAH molecular
289 ratios are listed in **Table 5**. Applied markers allow to distinguish between pyrogenic and petrogenic as well as traffic
290 and non-traffic sources of PAHs, namely: ANT/(ANT+PHE), FLT/(FLT+PYR), BaA/(BaA+CHR),
291 IPY/(IPY+BPE), CombPAH/15PAH and BaP/BPE. Calculated ratios for samples taken from residential and
292 industrial exhibited numbers that point to a domination of pyrogenically formed PAHs. The cross-plots of the PAH
293 ratios is depicted in **Fig. 3**

294 **Fig. 3** 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) (0.30-40) 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 (Wild and Jones 1995; 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 [^{14}C]PAH residues in soil under the stimulation of microbial activity, which obviously leads to unexpectable lower results while analyzing the concentrations of Naphthalene, Anthracene, Pyrene and Benzo(a)pyrene in soil samples (Eschenbach et al. 1998).

3.3 Statistical treatment of the data

Obtained probabilities for One-way ANOVA revealed statistically significant differences of 15PAHs and 7PAHs concentrations in soils between different land uses ($P \leq 0.05$). Plot of LS Means is depicted in **Fig. 4.**

Fig. 4. 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 FLU, PHE, FLT, PYR, BaA, CHR, BbF, BaP and BPE concentrations between parkland, residential and industrial areas ($P = 0.02-0.05$). 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. The results of the study proved the argument of difference in PAHs load on urban soils between studied sites. The land use factor is intensively expressed in distribution of the dominant individual PAHs, particularly BaP, PHE, FLT and PYR. These compounds are known to be a part of the PAHs mixtures isolated from the exhaust gases and industrial emissions (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 5**).

Fig. 5. Scale of potential sources of contamination with petroleum products (units per square km) with PHE distribution plots

3.4 Health risk evaluation of PAHs in soils

Health risk associated with soil contamination with PAHs was assessed using benzo(a)pyrene total potency equivalents approach (BaP$_{eq}$). The 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 (TEF), given in **Table 6**.

The calculated BaP$_{eq}$ on the average concentration of 15PAH (here and after referred to BaP$_{eq}$-15PAH) varied between 0.44 to 0.66 mg·kg^{-1} dry soil. The highest BaP$_{eq}$-15PAH 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 BaP$_{eq}$-15PAH (mean 0.44 mg·kg^{-1}). It is to be noted that one single sample taken from the Kirovskiy parkland exhibited a total 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 (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); Nadal et al. (2004) reported BaP$_{eq}$ concentrations varying between 0.02 to 0.12 mg·kg^{-1} in soils of Tarragona 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. 2013).

Finally, obtained BaP 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 safe level of 0.6 mg·kg^{-1} BaP$_{eq}$ (for each land use). The reported BaP$_{eq}$ of the 15PAH concentrations were above the safe level of 0.6 mg·kg^{-1}. Exposure to these soils through direct contact probably poses a significant risk to human health from carcinogenic effects of PAHs, even in urban parklands. Obtained values of BaP$_{eq}$ were further used to calculate index of incremental lifetime cancer risk (ILCR). This method provides quantitative evaluation of the human exposure to PAHs through various exposure scenarios via ingestion, dermal contact, and inhalation, of different age and gender groups.

The acceptable level of incremental lifetime cancer risk (ILCR) is set to of 10^{-6}-10^{-4} by the USEPA (USEPA, 2001). Risks below 10^{-6} do not require further action, while risks above 10^{-4} are considered to be of concern and require additional action to reduce the exposure and resulting risk (USEPA 2004). Calculated values of ILCR are summarized in **Table 7**.

All estimated ILCRs were within acceptable range (10^{-6}-10^{-4}). The ILCRs for different exposure pathways decreased in the order: ingestion > dermal contact > inhalation for all population groups. The greatest ILCR value was estimated for soil ingestion in case of residential land use ($4.25\cdot10^{-5}$), followed by industrial ($8.41\cdot10^{-6}$). Soil ingestion is considered to be more significant route of exposure in residential areas particularly for children, since they are more naturally active than other population groups, which leads to greater cancer risk caused by soil ingestion (Wang et al., 2015). The estimated cancer risks caused by dermal contact with soil and inhalation for all population groups were smaller than those caused by ingestion of soil particles, ranging from 10^{-6} to 10^{-12}. The applied RAIS model does not provide an estimation of cancer risk for youths, though this group of population is supposed to be more vulnerable for dermal contact with contaminated soil, which accounts for 32.5% of the exposure, followed by those for children and adults, accounting for 27.6% and 21.8%, respectively, suggesting that dermal contact could be a significant exposure pathway for youths compared to children and adults (Wang et al. 2015). Exposure route related to dermal contact with soil in industrial area was not assessed, considering that skin of the workers is not exposed and protected. This was due to the smaller skin surface areas in children, which led to smaller CRs caused by skin contacts.

4. Conclusions

Results of the study demonstrated that soils within studied urban areas are characterized by common levels of total 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. However application of RAIS cancer risk evaluation module revealed that incremental life time risks posed to population is under acceptable range (10^{-4}-10^{-6} and lower). One-way ANOVA results showed significant differences in levels of 15PAHs, 7PAHs, FLU, PHE, FLT, PYR, BaA, CHR, BbF, BaP and BPE between parkland, residential and industrial land uses, suggesting the influence of land use factor on distribution of PAHs in soils of the City. 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.

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569

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

Characteristics	Units	Primorskiy District	Vasileostrovskiy District	Kirovskiy 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

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

District	Land use	Soil name (WRB)	Mansell color chart index	TOC	N$_{tot}$	Clay	pH
				%			
Primorskiy	Parkland	Mollic Technosol	2.5 YR 4/1	4.10 ± 0.01	0.35 ± 0.06	5.83 ± 0.21	6.52
	Residential	Urbic Technosol	2.5 YR 4/1	3.82 ± 0.03	0.41 ± 0.08	7.43 ± 0.06	7.34
	Industrial	Urbic Technosol	10 YR 4/1	5.49 ± 0.02	0.23 ± 0.04	8.50 ± 0.10	7.15
Vasileostrovskiy	Parkland	Mollic Technosol	2.5 YR 4/1	5.39 ± 0.01	0.28 ± 0.07	7.3 ± 0.20	7.04
	Residential	Urbic Technosol	2.5 YR 4/1	6.41 ± 0.02	0.33 ± 0.05	1.87 ± 0.12	7.45
	Industrial	Urbic Technosol	5 YR 7/1	5.28 ± 0.02	0.29 ± 0.06	3.27 ± 0.15	7.76
Kirovskiy	Parkland	Mollic Technosol	2.5 YR 4/1	4.19 ± 0.03	0.32 ± 0.09	7.5 ± 0.10	6.84
	Residential	Urbic Technosol	5 YR 7/1	4.80 ± 0.03	0.30 ± 0.05	3.27 ± 0.15	7.12
	Industrial	Urbic Technosol	5 YR 7/1	3.09 ± 0.02	0.27 ± 0.04	7.67 ± 0.06	7.05

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 ($\alpha = 0.05$)
	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	0.00	0.42
ANA	0.02 ± 0.06	0.18	0.00	0.00	0.01	0.00	0.01	0.03	0.00	-
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	**0.04**
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	**0.04**
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	**0.05**
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	**0.05**
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	**0.04**
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	**0.04**
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	**0.05**
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	**0.04**
∑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	**0.05**

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(ah)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(ah)anthracene.

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

Location	Study area	Concentrations (mg·kg^{-1} d.w.)	∑PAH	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 Orlean, 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/∑ PAH	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}, $mg \cdot kg^{-1}$

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
∑15PAH	0.4435	1.84154	0.05191	0.65531	1.31631	0.02644	0.55004	1.3854	0.0928	
∑7PAH[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).

Table 7. Calculated IACRs based on different routes of exposure and land use scenarios (all age groups)

Land use scenario	Route of exposure	Life time cancer risk (unitless)			
		Ingestion	Dermal	Inhalation	Total risk
Parkland		$6.16 \cdot 10^{-7}$	$1.71 \cdot 10^{-7}$	$2.05 \cdot 10^{-12}$	$7.77 \cdot 10^{-7}$
Residential		$4.24 \cdot 10^{-5}$	$1.24 \cdot 10^{-6}$	$2.83 \cdot 10^{-8}$	$4.36 \cdot 10^{-5}$
Industrial (composite worker)		$8.41 \cdot 10^{-6}$	-	$1.98 \cdot 10^{-7}$	$8.61 \cdot 10^{-6}$
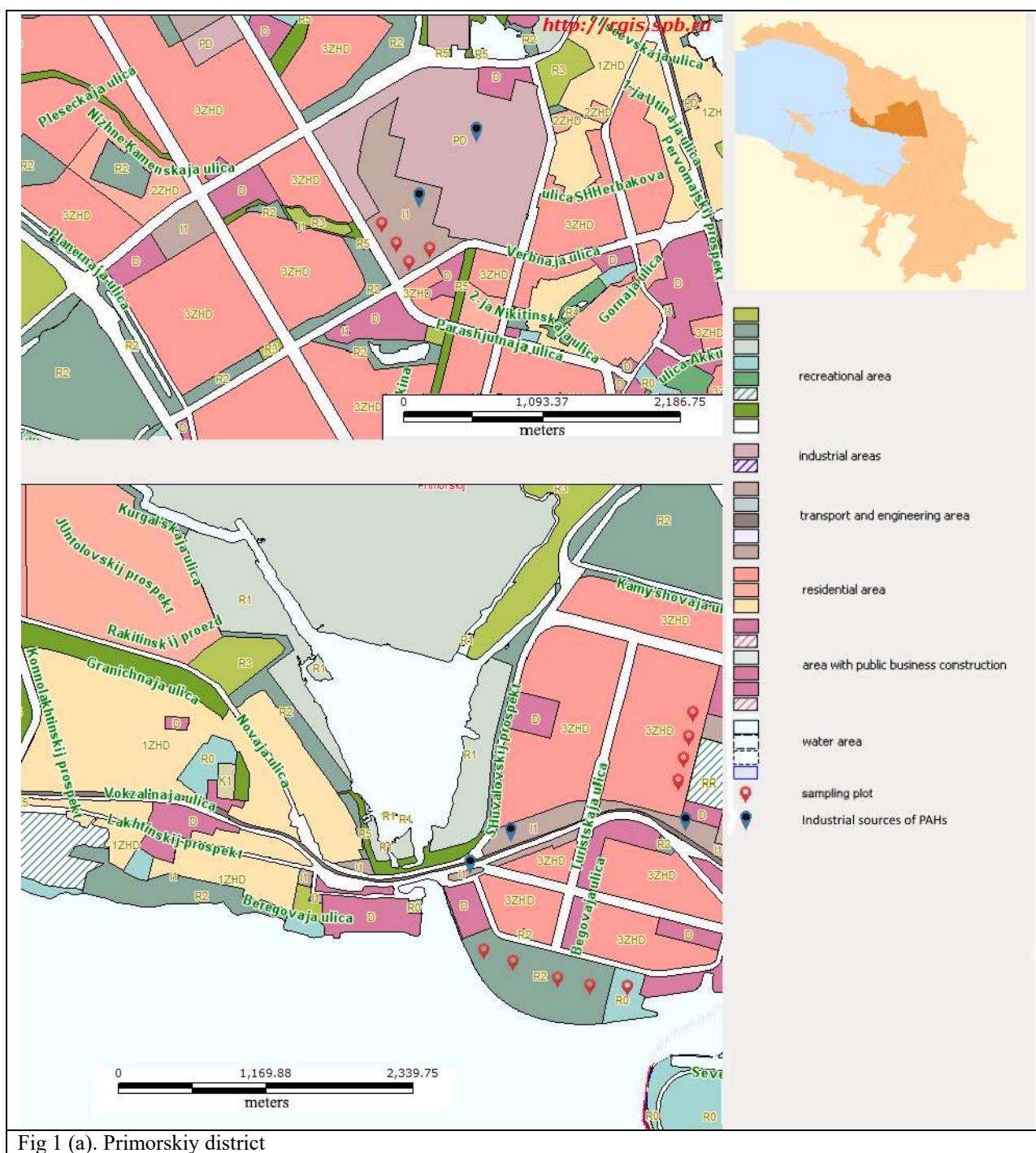
Fig 1 (a). Primorskiy district
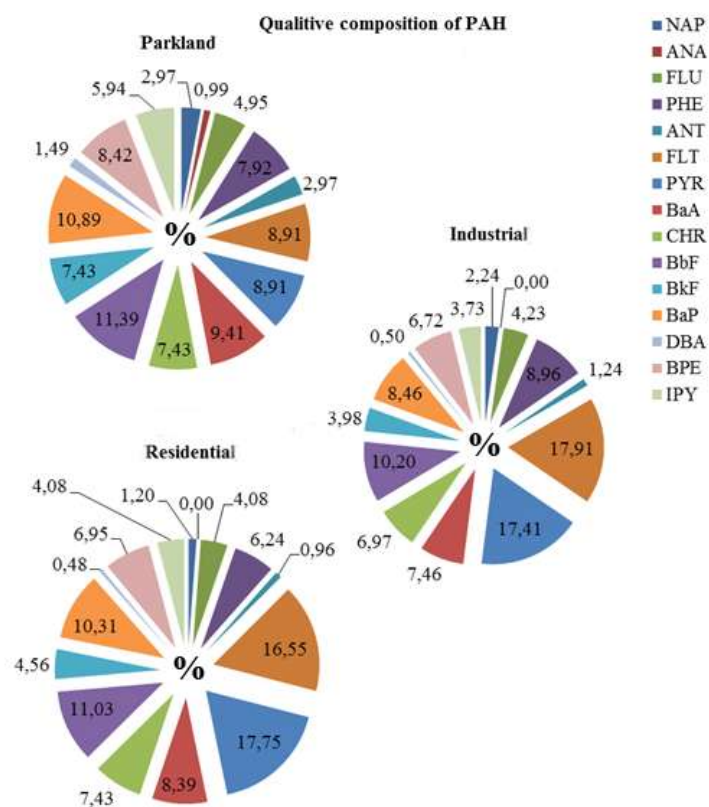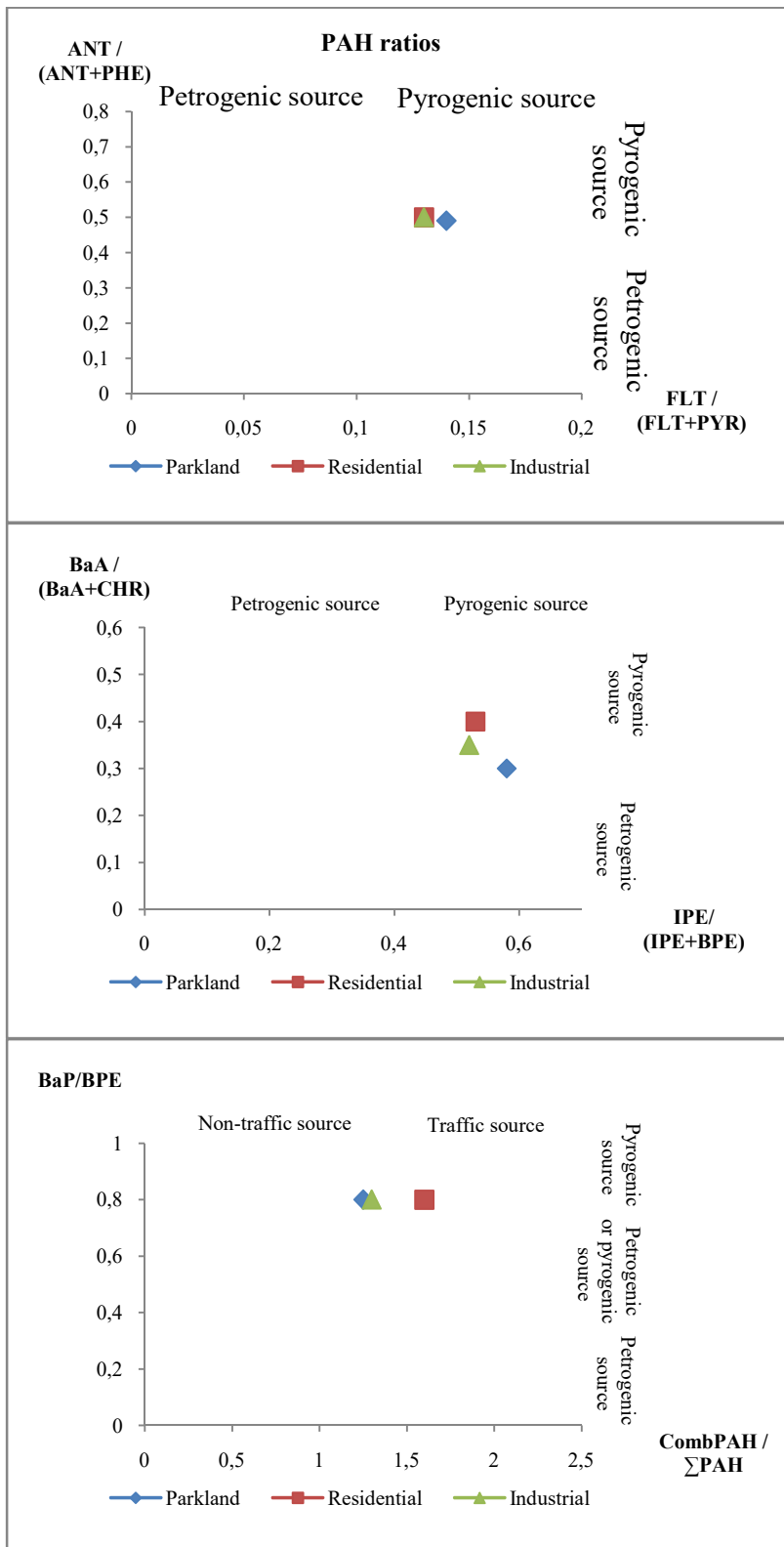
Fig. 1 (b). Vasileostrovskiy district
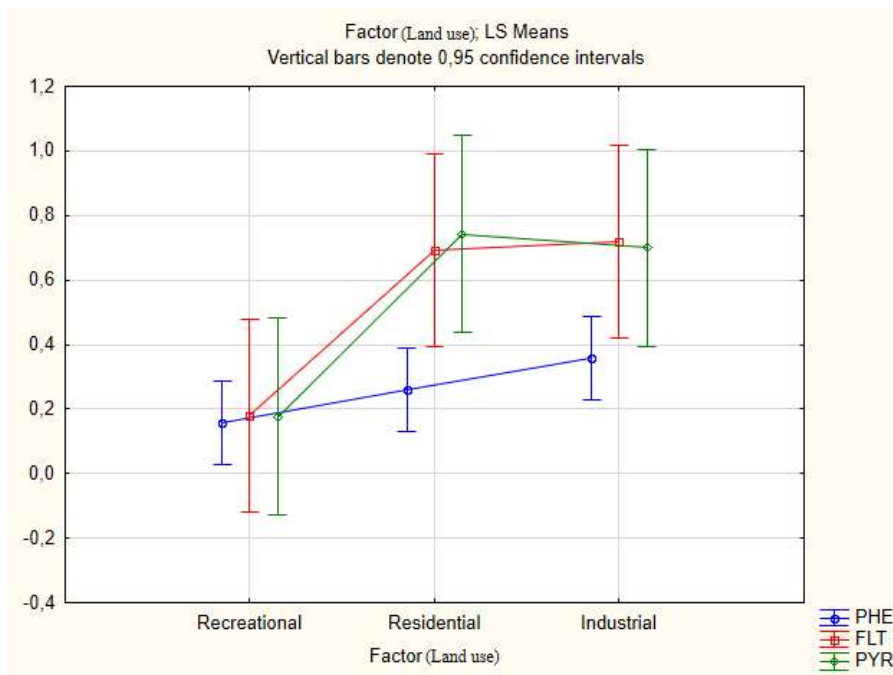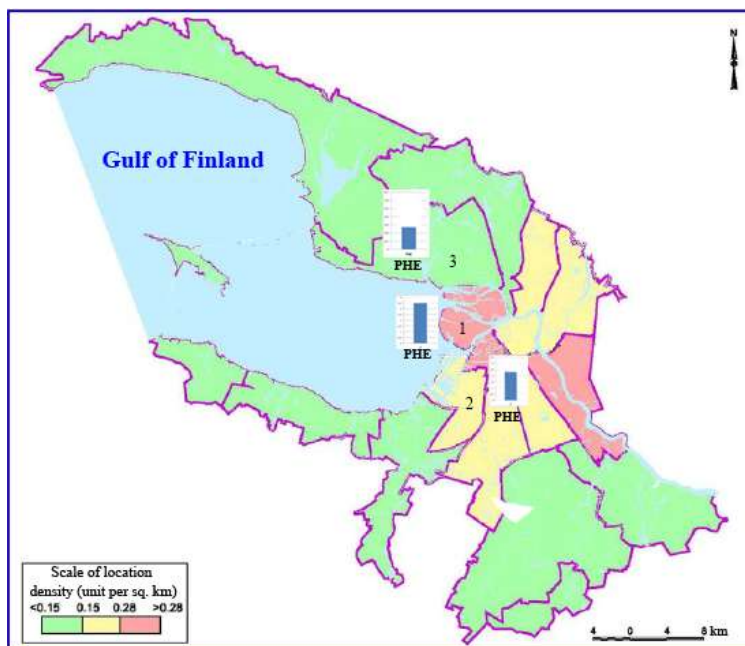

Fig. 1 (c). Kirovskiy district
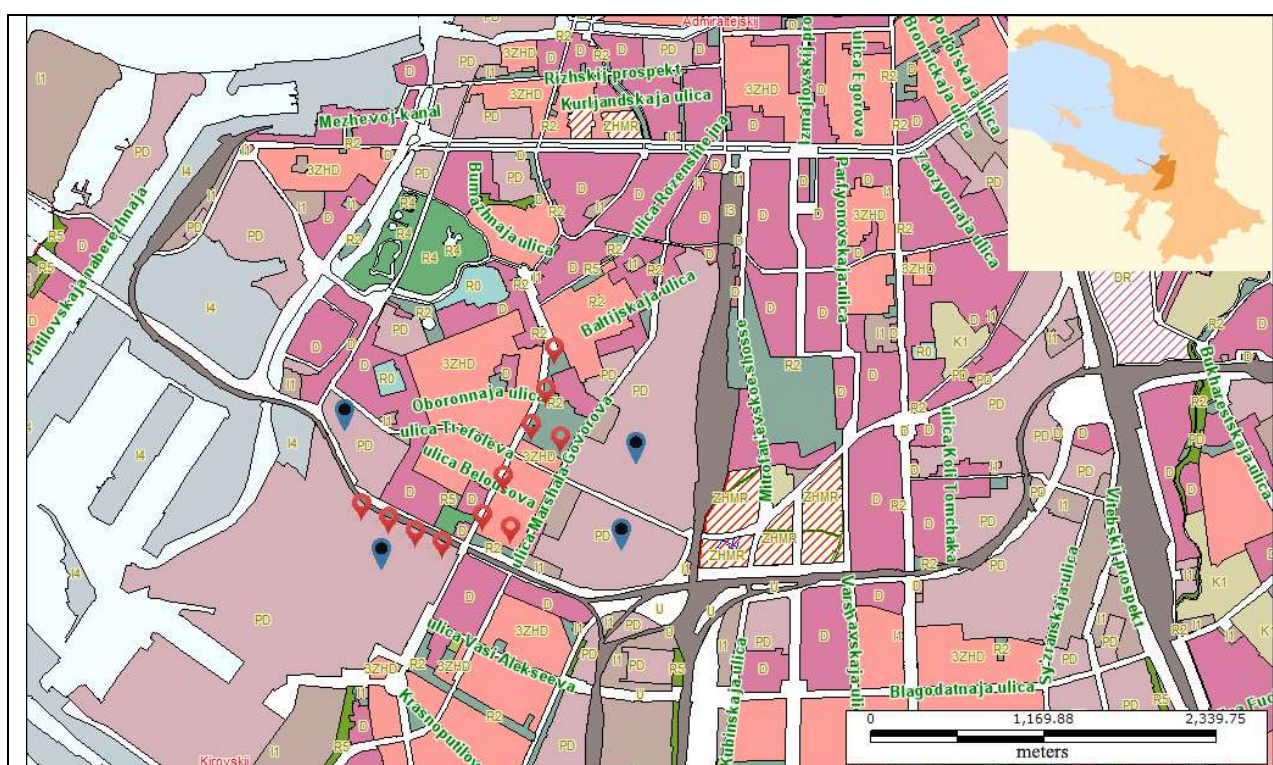
Fig. 2 Composition of PAH mixtures in studied soil

Fig. 3. PAH source apportionment

Fig 4. LS Means plot, differences of PAH levels in soil between land uses

Fig. 5. Scale of potential sources of contamination with petroleum products (units per square km) with PHE distribution plots