Urban soil quality assessment in green areas of two medium-sized Finnish cities, Lahti and Joensuu

Alina Kamalova[1*], *Leisan* Akhmetzyanova[1], and *Polina* Galitskaya[1]

[1]Kazan Federal University, Kazan, 420008, Russia

Abstract. In this study, contamination levels and ecotoxicity in 29 urban soils in two medium-sized Finnish cities, Lahti and Joensuu were evaluated. It was established that Cd concentration exceeded the natural background level in all soils tested. The estimated number of soil samples contaminated with Pb, Ni, Cu and Zn was 1, 3, 1 and 23 respectively. The total content of polyaromatic hydrocarbons (∑16PAH) was analyzed in urban soil samples. It was found that in soils ∑16PAH ranged from 23.78 to 831.42 ng*g^{-1} (Lahti) and from 14.38 to 1173.95 ng*g^{-1} (Joensuu). No correlation was found between the levels of total metals and total PAHs. Ecotoxicity was analyzed by bioassay of elutriate using Paramecium caudatum (R = 0.75). The ecotoxicity index levels (LID10) ranged from 1 to 40. A strong correlation was observed between total metal content and soil ecotoxicity levels.

1 Introduction

The interplay between urbanization and environmental health has been increasingly scrutinized with a particular focus on the accumulation of polycyclic aromatic hydrocarbons (PAHs) and metals in urban park soils - a phenomenon with profound implications for public health and ecological integrity. Urban parks, often considered oases within the concrete landscape, are not immune to the infiltration of contaminants such as benzo[a]anthracene, chrysene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene (together known as PAHs – polyaromatic hydrocarbons), as probable human carcinogens and metals such as cadmium (Cd), lead (Pb), aluminum (Al), arsenic (As), and others, whose presence at elevated levels can lead to toxicological challenges for both humans and wildlife [1]. These metals, by virtue of their non-biodegradability and potential for bioaccumulation, present a silent threat that necessitates vigilance [2]. PAHs have been listed as priority pollutants by both the US Environmental Protection Agency (EPA) and European Union (EU) [3]. While PAHs can occur naturally, mostly they are originated from anthropogenic processes, such as burning of fossil fuels and other organic substances. PAHs containing two or more rings usually have high stability in the environments [4-5].

* Corresponding author: akhtjamovaalina07@gmail.com

City green spaces provide benefits for human inhabitants, and soil, being a vital constituent of the urban environment, performs numerous ecological, social and economic functions [6-7]. In urban areas, intensive human activities and traffic are the main sources of metals that pollute parks and roadside lawns. They can detrimentally alter soil chemistry, impede plant growth, and disrupt the delicate balance of urban ecosystems. For these reasons, urban soil is a good indicator of the level and extent of metal accumulation in the surface environment [8].

In Joensuu and Lahti, two Finnish cities with distinct industrial histories and urban landscapes, the study of soil contamination acquires a specific significance. Joensuu, with its proximity to various water bodies and a history intertwined with the forestry industry, contrasts with Lahti's more diverse industrial background, providing a unique comparative framework for assessing how different urban profiles influence soil quality. Both cities exemplify the broader Finnish commitment to environmental sustainability, yet they underscore the persistent challenge of managing urban industrial legacies within green spaces. In examining the PAHs and metal content within their parklands, this study aims to contribute not only to local urban management strategies but also to the global discourse on urban environmental health, offering insights into the complex interrelations between industrial development, urban planning, and environmental conservation. The analysis of this pollutants in this study is pivotal, for it not only assesses current conditions but also facilitates a predictive understanding of potential ecotoxicological trajectories, offering a basis for proactive measures in urban environmental management and public health policy.

2 Materials and methods

2.1 Study site and soil sampling

This research was carried out in two Finnish cities: Lahti (60°58'54"N 25°39'53"E) and Joensuu (62°36'19"N 29°45'36"E). Lahti is situated in the southern part of Finland and approximately 100 km (60 miles) north-east of the capital, Helsinki. Experiences a temperate climate characterized by cold winters and mild summers with the average daily temperature in July exceeding over 23°C. Lahti with a population of 120,700 inhabitants, is known for its proximity to natural landscapes: green areas cover 75% and water bodies 10% of Lahti's surface area. Thus, there is 250 m^2 of green space per citizen. Joensuu is located in eastern of Finland, shares a similar temperate climate with Lahti. Positioned about 460 km north of Helsinki, Joensuu is a smaller city with a population of 77,513 residents. Despite its smaller size the Joensuu 80% of the area is forests, and have 778 lakes.

The soil sampling occurred in June-July 2021 involved systematic sampling from 14 parks of Lahti and 15 green zones of Joensuu which selected randomly and situated in different districts of these cities. The characteristics of parks and public gardens both cities are listed in Table 1. Soils and dust (10-20 g) were taken from the upper layer of the soil cover (from 0 to 5 cm) at three equidistant points: the right corner, middle and left corner of the main/south entrance of each park. Samples were ground in a mortar and removal of unwanted content (stones, plant material, etc.) and passed through a sieve with a hole diameter of 1 mm.

Table 1. Characteristics of urban green areas at the two Finnish cities – Lahti and Joensuu.

No.	City	Park name	Address	Location coordinates
1	Lahti	Mytäjäisten uimaranta	Mytäjärvi, 15800 Lahti	60°58'41.1"N 25°38'13.1"E
2		Ankkurin rantapuisto	Tyyrpuurinkatu 7	61°00'04.6"N 25°38'54.9"E
3		Pallaksenpuisto	Rullakatu 10, 15900 Lahti	60°59'27.9"N 25°37'39.2"E
4		Fellmanninpuisto	Paasikivenkatu, 15110	60°59'03.8"N 25°38'42.9"E
5		Launeen keskuspuisto	Kaarikatu 26	60°58'18.6"N 25°38'54.1"E
6		Koulupuisto	Kirkkokatu 1, 15110 Lahti	60°59'08.1"N 25°39'14.6"E
7		Kirkkopuisto	Kirkkokatu	60°59'07.9"N 25°39'28.4"E
8		Marianpuisto	Mariankatu 4	60°58'10.5"N 25°40'13.6"E
9		Radiomäki	Radiomäenkatu 20	60°58'44.2"N 25°39'09.0"E
10		Esikkopuisto	Nikkarinkatu	60°58'01.0"N 25°40'10.5"E
11		Osmolanpuisto	Huovilankatu 7	60°58'29.1"N 25°39'12.3"E
12		Green area next to Lahden Lyseo (school)	Lahdenkatu 6	60°59'07.6"N 25°39'06.1"E
13		Historiallinen Museo	Kartanontie 1, 15110	60°59'08.1"N 25°39'04.5"E
14		Pikku-Vesijärven puisto	Kariniemenkatu	60°59'22.5"N 25°39'06.9"E
15	Joensuu	Ristipuiston leikkipaikka	Pohjoiskatu 9	61°12'34.7"N 26°02'39.4"E
16		Säkkijärvenkujan leikkipaikka	Säkkijärvenkuja 12, 80200	62°35'34.7"N 29°47'40.5"E
17		Ruusupuisto	80220 Joensuu	62°35'21.5"N 29°44'51.3"E
18		Kanavapuiston leikkipaikka	80100 Joensuu	62°36'09.1"N 29°46'03.2"E
19		Jääkärinpuisto	Rantakatu 2, 80110	62°35'42.1"N 29°45'29.5"E
20		Kirkkopuisto	Koulukatu 7	62°35'40.0"N 29°45'04.7"E
21		Sirkkalanpuisto	Sirkkalan Silta, 80100	62°36'06.0"N 29°46'19.3"E
22		Niinivaaran koirapuisto	Niinivaarantie 23, 80200	62°35'36.8"N 29°47'01.9"E
23		Korpiselänpuiston leikkipaikka	Korpiselänkatu 5	62°35'41.7"N 29°47'12.8"E
24		Keskuspuisto	80100 Joensuu	62°36'06.0"N 29°45'34.5"E
25		Niinivaaran kenttä	Loimolankatu 12, 80200	62°35'43.2"N 29°47'39.3"E
26		Eteläinen rantapuisto	Rantakatu 9a, 80100	62°35'51.8"N 29°45'43.8"E
27		Pohjoinen rantapuisto	80100 Joensuu	62°35'56.0"N 29°45'53.9"E
28		Vapaudenpuisto	Rantakatu 20	62°36'01.0"N 29°45'51.9"E
29		Eliel Saarisenpuisto	80100 Joensuu	62°36'00.8"N 29°45'59.4"E

2.2 Metals content in soils samples

The granulometric composition of the soil samples was determined in accordance with ISO 13320:2009, based on the relative content of sand, silt and clay fractions according to Atterberg [9]. A soil samples from Lahti are classified mainly as loamy sand, while those

from Joensuu as sandy loam. All the soils showed pH around neutrality ranged from 6.9 to 7.8.

Metals such as aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), selenium (Se), strontium (Sr) and zinc (Zn) were evaluated in this study (results shown in Supplement Table 1) (49).

Metals have maximum permissible level (MPL) in soils set by various authorities. In this study, the standards used by WHO/FAO [10] and Finnish threshold values for potentially harmful elements (Decree 214/2007) [11] were adopted.

The Contamination Factor (CF) was defined as the concentration of a metal in contaminated soil divided by the normal value in an uncontaminated environment (background values) [12-13], according to the following ratio:

$$CF = \frac{Contamination\ factor\ metal\ content}{Base\ metal\ value} \quad (1)$$

The total technogenic pollution index (*Zc*) was calculated and estimated on the scale according Saet et. al. [14, 15] , the formula used to calculate the indices are presented below:

$$Z_c = \sum_{i=1}^{n} CF - (n-1) \quad (2)$$

Where *Zc* is the total technogenic pollution index; *n* is the number of pollutants; *CF* is the concentration coefficient of the *i*-th pollutant, which is equal to the degree of exceedance of its background content.

Before the estimation soils were air dried till the constant weight. For the determination of metals concentration in the urban soil the homogenized samples (0.5 g) were accurately weighed into 50 ml Falcon poly(propylene) centrifuge tubes (pre-cleaned with 10% nitric acid followed by repeated rinsing with bidistilled water) and 20 ml of 0.1 M HNO_3 solution added to the tubes. The tubes were shaken on a shaker at 200 °C with a rotation speed of 30 ± 1 rpm for 24 h. In each batch, a blank sample containing the same reagents was also subjected to the extraction procedure. The extracts were kept in a fridge at 4°C prior to ICP-AES (ICPE-9000, Shimadzu) analyses [16].

2.3 PAH content in soil samples

Individual solutions at 200 µg/mL (in acetonitrile) of naphthalene (Nap), 2-methylnaphthalene (2-MNa), biphenyl (Biph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP) and 100 µg/mL dibenz(a,h)anthracene (DbA) and benzo(g,h,i)perylene (BgP), was purchased from Ekros-Analitika (Saint Petersburg, Russia) and were used for optimization the extraction procedures [17]. All solvents used were all analytical grade and the water was purified with Sartorius arium® comfort system (Germany).

Extraction recovery of individual compound was evaluated the following analytical procedure (additional control). The mean recoveries were 63.3% (Nap), 49.2% (2-Mna), 88.7% (Biph), 56.5% (Acy), 60.8 (Ace), 53.4% (Flu), 42.1% (Phe), 63.4% (Ant), 69.5% (Fla), 67.4% (Pyr), 52.7% (BaA), 46.1% (Chr), 74.6% (BbF+BkF), 59.1% (BaP), 74.9%

(DbA), 61.9% (BgP). Limit of detection (LOD) was calculated as three times the noise level of the chromatogram in blank sample.

The 5 g soil sample was transferred into a 50 mL glass tumbler and 25 mL of chloroform was added, then shaken vigorously for 1 min. The samples were ultrasonicated for 60 min at 22.5°C. The extraction solution was filtered into a 500 ml vacuum flask, then were concentrated to 1 mL by rotary vacuum evaporation, was washed with 4 ml of chloroform and transfer into a 15 mL clean tube. Then, the upper layer of the prepared samples was filtered through Minisart RC 0.20 μm syringe filter (Sartorius, Germany) and transfer 1.5 mL extract to an autosampler vial.

The experiment included additional controls (5 g), model soil samples with PAHs solution 80 ng each component which were subjected to similar extraction steps as the studied samples. Soil contamination with PAHs was assessed according to the classification of Maliszewska-Kordybach, based on the 16 USEPA priority pollutants [18-19].

2.4 GC/MS analysis of PAHs

The determination of PAHs was performed on GCMS-TQ8040 (Shimadzu) with splitless injection. The capillary column Rxi5Sil MS (30 m × 0.25 mm × 0.25 μm) was used for separations. Helium (99.999%) was used as the carrier gas. A volume of 1 μL was injected in the split mode with a flow ratio of 10:1, and the injector temperature was maintained at 300°C. The oven temperature program was as follows: initial temperature of 70°C was held for 2 min, ramped to 150 °C at 25 °C/min, then increased to 200°C at a rate of 3°C/min and finally increased to 280 °C at a rate of 8°C/min and held for 11 min. A multiple reaction monitoring (MRM) was used for the qualitative determination of PAHs.

2.5 Ecotoxity assay

To evaluate soil toxicity used the biotest method on the protozoan *Paramecium caudatum* [20]. The elutriates (soil: cultivation water in 1:10 ratio by mass, 6-hour stirring at room temperature conditions, and 12-hour sedimentation) were prepared for toxicological testing on *P. caudatum*. After the elutriates preparation, it was centrifuged for 30 min by 3500 g and filtered. The produced elutriate was diluted 1:1, 1:4 with cultivation water. Dilution (aquarium) water was used as a control sample. Toxicity tests were incubated at 20°C and constant illumination. The mortality rates (I, %) were determined as the ratio of the immobilized test-organism count compared to their initial counts. In case if I, % was 10% or above, a series of dilutions was prepared and the LID10 (lowest dilution of the elutriate/sample) was calculated using the linear interpolation method [21]. The eluate was considered non-toxic if LID10 was equal to 1.

2.6 Statistical analysis

All measurements were conducted in three replicates. Concentrations of metals were expressed as mean ± SD (Standard Deviation). Statistical significance of differences was analyzed using non-parametric criteria such as Fisher test (α=0.05). Statistical analysis was performed in Statistica 10.0 software (StatSoft, USA). Graphs were prepared using Microsoft Excel 2021 (Microsoft, USA).

3 Results and Discussion

3.1 Metals content in soils sampled in green areas in Lahti and Joensuu

The concentrations of Cu, Pb, Zn, Ni, and Cd in the urban soils of Lahti and Joensuu are presented in Table 2. These metals were selected as representative contaminants of urban soil due to traffic pollution [22]. It is well known that Cu, Pb, and Zn are primary markers of traffic pollution. Specifically, Cu is emitted by vehicle brakes, Pb is associated with coarse particles from vehicular exhausts, and Zn originates from tire wear [23].

The maximum Cu concentration was found in park No. 4 of Lahti, reaching 54.10 $mg*kg^{-1}$, with the lowest concentrations in samples No. 5 and 14 (Lahti). Additionally, high levels of Co, Fe, and Mn were observed (Supplement Table 1) (49). In Joensuu's green zones, Cu concentrations ranged from 0.09 to 20.98 $mg*kg^{-1}$, all below the MPL of 100.0 $mg*kg^{-1}$ set by WHO/FAO and Finnish regulations (100.0 $mg*kg^{-1}$) [10].

The highest Pb concentration was recorded in sample No. 6 (Lahti). In Joensuu, Pb concentrations in parks and public gardens were minimal or zero (No. 25), except for sample No. 26 (3.95 $mg*kg^{-1}$), taken near a road. Lu et al. (2003) noted that urban soil Pb levels often exceed pollution evaluation criteria (57.4 $mg*kg^{-1}$), except in some urban parks. The mean Pb concentration is highest in roadside soils, suggesting vehicle emissions as the main source [16]. These values are within the limits set by WHO/FAO and the Finnish Ministry of the Environment (Table 2).

Zn concentrations in Lahti park soils ranged from 22.78 to 74.24 $mg*kg^{-1}$, while in Joensuu, they varied from 33.23 to 97.50 $mg*kg^{-1}$. The highest Zn concentration was in sample No. 25 (Joensuu), and the lowest in No. 9 (Lahti). Sample No. 25 (Joensuu) also showed increased levels of Fe (18,550 $mg*kg^{-1}$), Cr (25.18 $mg*kg^{-1}$), and Al (4,777.5 $mg*kg^{-1}$) (Supplement Table 1) (49). These Zn values did not exceed the thresholds set by WHO/FAO and the Finnish Ministry of the Environment (Decree 214/2007) [10, 11]. Bahiru et. al. (2019) reported Zn concentrations in soils ranging from 60.09 to 414.12 $mg*kg^{-1}$, compared to a natural range of 10 to 300 $mg*kg^{-1}$ [24, 25].

The estimated Cd concentrations ranged from 0.16 to 1.00 $mg*kg^{-1}$ in Lahti and from 0.06 to 1.46 $mg*kg^{-1}$ in Joensuu (Table 2). The highest values were in sample No. 27 (Joensuu), from a playground near a lake, below the MPL of 3.0 $mg*kg^{-1}$ set by WHO/FAO. Finnish regulations specify a Cd threshold of 1 $mg*kg^{-1}$ in soil. In Lahti, only sample No. 13 reached this threshold, while in Joensuu, samples No. 24, 27, and 29 were exceptions.

As shown in Table 2, the soil concentration of Ni in this study was within ranges with values ranging between 3.78-12.43 $mg*kg^{-1}$ to 4.23-21.80 $mg*kg^{-1}$, for Lahti and Joensuu, respectively. In general, the average values of Ni content in both Finnish cities were 5 times less than those established by WHO/FAO and Finnish threshold values [10-11].

Ni concentrations were between 3.78 and 12.43 $mg*kg^{-1}$ in Lahti and 4.23 and 21.80 $mg*kg^{-1}$ in Joensuu (Table 2). On average, Ni content was five times lower than the limits established by WHO/FAO and Finnish standards. Nikiforova et al. (2022) reported higher Ni concentrations in industrial districts of Moscow (30.7 $mg*kg^{-1}$), Cu is 329 $mg*kg^{-1}$, Zn is 150 $mg*kg^{-1}$, As is 6.34 $mg*kg^{-1}$, Cd is 0.93 $mg*kg^{-1}$ and Pb is 143 $mg*kg^{-1}$ compared to recreational districts (~3.5 times lower) [26]. In the million-plus city of Kazan and its satellite city Zelenodolsk, the Ni content ranged from 7.09 to 24.33 $mg*kg^{-1}$ and from 4.40 to 19.33 $mg*kg^{-1}$, respectively [27].

Thus, summarizing, high metal pollution was noted in green zone No. 7 (Lahti), with increased concentrations of Ni, Al, As, Co, Cr, Fe, Mn, Se, and Sr, and in No. 6 (Lahti), with high levels of Pb, Zn, Co, Cu, Mn, and Se (Supplement Table 1) (49). The highest metal concentrations were found near heavily trafficked motorways. Notably, sample No. 5

(Lahti) had high levels of Cd (0.97 mg*kg^{-1}) and Ni (6.73 mg*kg^{-1}), but low Cu (0.8 mg*kg^{-1}).

In Joensuu, sample No. 24 had high concentrations of Cr (30 mg*kg^{-1}), Fe (22,550 mg*kg^{-1}), Mn (65.4 mg*kg^{-1}), Ni (21.8 mg*kg^{-1}), and Al (54.25 mg*kg^{-1}), with no As detected, likely due to its proximity to a parking lot.

The lowest values across six metals were in No. 11 (Lahti), taken from a children's playground near the railway. In No. 28 (Joensuu), located near the town hall and a parking lot, there were low contents of eight metals: Cu, Zn, Ni, Mn, Fe, Cr, Co, and Al.

Table 2. Concentration of metals (mg*kg^{-1}) in soils sampled in green areas in Lahti and Joensuu.

No.	City	Cd	Cu	Pb	Ni	Zn
1	Lahti	0.19±0.05[c]	1.37±1.7	0.48±0.11	7.25±0.74	34.4±5.94
2		0.56±0.63	3±2.53	3.75±2.65	6.73±1.91	39.7±1.03
3		0.98±0.18	1.05±0.74	2.6±1.98	6.1±2.09	36.4±5.48
4		0.4±0.19	54.1±1.78	0.7±0.49	4.9±0.18	30.2±6.29
5		0.97±0.01	0.8±0.87	2.55±1.34	6.73±0.21	28.6±1.24
6		0.61±0.46	14.6±3.39	8.88±4.07	7.78±1.06	74.3±0.96
7		0.81±0.21	3.78±0.08	1.75±1.24	12.43±2.26	30.8±2.76
8		0.54±0.48	2.26±1.6	4.15±4.53	5.43±0.14	34.9±3.58
9		0.63±0.44	5.3±3.75	3.25±2.3	5.7±2.23	22.8±5.76
10		0.57±0.44	2.75±1.87	1.4±0.99	6.33±0.78	29±0.85
11		0.85±0.06	1.56±1.1	4.38±1.31	3.78±0.78	36.6±6.19
12		0.16±0.18	3.48±2.36	0.75±0.35	4.55±0.67	35.6±5.02
13		1±0.18	0.36±0.25	2.35±2.33	6.95±1.17	33.9±1.2
14		0.98±0.18	-	1.55±1.1	4.53±1.63	27.8±4.45
15	Joensuu	0.06±0.07	4.79±0.72	-	10.92±0.53	51±14.46
16		0.19±0.18	8.55±5.38	-	9.79±2.55	52.6±25.74
17		0.34±0.24	10.05±2.97	-	10.44±0.71	43.1±17.96
18		0.06±0.06	3.13±2.21	-	7.89±0.14	44.2±0.74
19		0.12±0.16	11.38±0.53	0.43±0.18	13.42±0.18	53.5±0.35
20		0.26±0.03	11.85±0.5	-	16.29±0.2	59.3±0.5
21		0.86±0.48	14.45±1.98	-	14.67±3.08	35.3±5.73
22		0.14±0.1	12.65±0.78	-	18.84±0.07	53±1.06
23		0.07±0.06	7.05±2.69	-	13.12±3.01	53.3±2.83
24		1.05±0.15	20.98±3.29	2.8±1.98	21.8±3.78	58.8±10.25
25		0.37±0.02	10±3.18	-	14.08±1.48	97.5±28.99
26		0.44±0.47	14.28±0.67	3.95±0.92	18.9±0.18	69.3±2.47
27		1.46±0.34	10.48±3.15	2.63±0.88	12.68±1.13	44.8±3.89
28		0.12±0.11	0.09±0.06	0.7±0.49	4.23±0.49	33.2±3.36
29		1.44±0.18	17.28±0.25	2.43±1.17	14.2±0.53	93.3±3.18
MPL[a] (WHO / FAO)		3	100	100	50	300
Finnish threshold[b]		1	100	60	50	200
Natural (background) concentration[b]		0.03	22	5	17	31

[a] MPL [10]; [b] Finnish limits, according to Ministry of the Environment, Finland, Government Decree 214/2007 [11]; [c] ±SD - standard deviation

The CF index reflects the level of soil contamination by metals. It is calculated by comparing the actual concentrations of metals with those considered safe for the environment (e.g., natural background levels) [11, 28]. A CF exceeding 1 indicates the presence of anthropogenic contamination, while a CF exceeding 6 denotes a high level of contamination [29–31]. Cd was identified as the predominant pollutant in the park soils of both cities (Supplement Table 2) (49). In Lahti, the CF level for Cd exceeded 6 in all samples, except for sample No. 12. In Joensuu, most soils (No. 16, 17, 20, 21, 24, 25, 26, 27, 29) were highly contaminated, while No. 19, 22, 28 were considerably contaminated, and No. 15, 18, 23 were moderately contaminated by Cd. Soils from Lahti and Joensuu showed no contamination with Cu (CF < 1), except for No. 4 (Lahti), which was moderately contaminated. Regarding Pb and Ni, all samples from Lahti and Joensuu were uncontaminated (CF < 1), except for samples from Lahti (No. 6) and Joensuu (No. 22, 24, 26), which were moderately contaminated. Moderate Zn contamination was found in samples No. 1, 2, 3, 6, 8, 11, 12, 13 (Lahti), and in all samples from Joensuu (1 < CF < 3). Samples No. 4, 5, 7, 9, 10, 14 (Lahti) were classified as practically uncontaminated (CF < 1).

The Total Contamination Index (Zc), calculated using the Saet equation for five metals, characterizes the overall level of metal contamination in park soils. According to the soil pollution hazard estimation scale [32-33], Zc values showed that No. 1, 12 (Lahti), and No. 15, 16, 18, 19, 22, 23, 28 (Joensuu) were within permissible contamination limits. No. 4 (Lahti) and No. 17, 20, 25, 26 (Joensuu) exhibited low contamination, while No. 2, 6, 7, 8, 9, 10, 11 (Lahti) and No. 21 (Joensuu) were moderately polluted. Highly dangerous contamination by metals included samples No. 3, 5, 13, 14 (Lahti) and No. 24, 27, 29 (Joensuu), with the Zc index in Joensuu being 1.5 times higher than in Lahti.

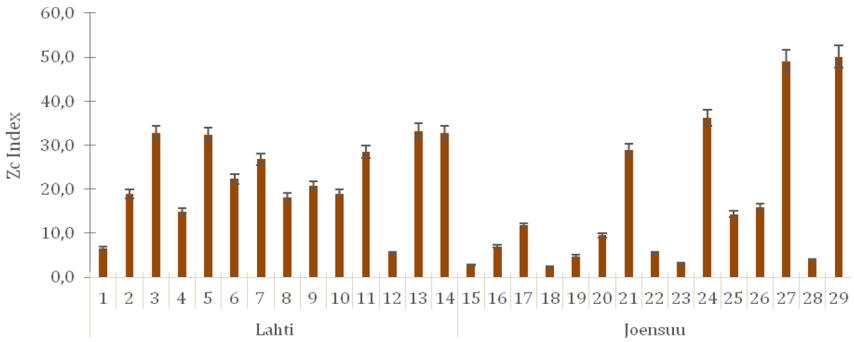

Fig. 1. Total contamination index (Zc) for metals in soils from Lahti (No.1 – 14) and Joensuu (No.15-29).

3.2 PAH content in soils sampled in green areas in Lahti and Joensuu

Tables 3 and 4 summarize the concentrations of each PAH and their total (∑16PAH) in the soils studied in the two cities.

The total concentration of 16 PAHs (∑16PAH) in Lahti's parks and squares ranged from 23.78 to 831.42 ng*g^{-1} (mean 280.70 ng*g^{-1}) (Table 3). The highest level of ∑16PAH contamination was observed in soil sample No. 7 (Lahti), likely due to its location next to traffic areas. Notably, this sample contained high levels of PAHs considered carcinogens by the US Environmental Protection Agency, such as BkF (111.29 ng*g^{-1}), BaP (43.66 ng*g^{-1}), and DbA (57.03 ng*g^{-1}) [3, 34].

Lahti has transitioned from coal to obtaining electricity and heat from waste or residual forest industry products [35], resulting in no large industrial zones within the city. The

lowest ∑16PAH values were found in sample No. 8 (Lahti) – 729.09 ng*g^{-1}. These values are comparable to those in the literature; for instance, Crnković et al. (2006) reported ∑16PAHs values of 0.298 mg*kg^{-1}, 0.375 mg*kg^{-1}, and 0.018 mg*kg^{-1} in residential, urban, and rural zones of Belgrade, Serbia, respectively [36].

In Joensuu, a wide range of soil ∑16PAH concentrations was observed, ranging from 14.38 ng*g^{-1} to 1173.95 ng*g^{-1} (mean 323.09 ng*g^{-1}) (Table 4). The maximum pollution level was in sample No. 24 (Joensuu), characterized by high traffic near a fairground, large shops, a central park, and parking areas. This sample had high levels of carcinogenic PAHs, such as BkF (193.06 ng*g^{-1}), BaP (93.33 ng*g^{-1}), and DbA (135.88 ng*g^{-1}) [1]. Soils near bridges (No. 21) and roads (No. 22) in Joensuu also showed high concentrations – 942.15 and 793.73 ng*g^{-1}, respectively. Parajuli et. al. (2017) also presented results of research impact of PAHs on the environmental microbiome, as well as adverse health outcomes and human immunity [37].

According to Maliszewska-Kordybach (1996), samples No. 3, 7, 8 from Lahti were classified as moderately contaminated, No. 5, 6, 10, 14 as slightly contaminated, and the remaining samples (No. 1, 2, 4, 9, 11, 12, 13) as not contaminated [18]. In Joensuu, sample No. 24's ∑16PAH level was 173.95 ng*g^{-1} higher than the heavy pollution threshold (1.0 mg*kg^{-1}), indicating that the surface soils in this zone stored a significant amount of PAHs. Thus, No. 24, 18, 21, 22 in Joensuu's parks were classified as moderately contaminated, No. 19, 26 as slightly contaminated, and samples No. 15, 16, 17, 20, 23, 25, 27, 28, 29 as not contaminated with PAHs.

The Zc index for metals in soils from this study showed no correlation with ∑16PAH results for the 29 parks and green zones in Lahti and Joensuu (r = 0.17). The low correlation coefficient may be due to the different sources of these pollutants. Metals occur naturally from weathering of parent materials and from anthropogenic sources such as traffic emissions (mainly Pb and Cd), industrial activities, and infrastructure repairs, while PAHs are often linked to combustion processes and the processing of organic materials like petroleum products, coal, wood, and garbage [38–40]. The disparate sources mean that the levels of these pollutants in the soil can vary significantly and independently of each other.

Table 3. Concentrations of polycyclic aromatic hydrocarbons (PAH) (ng*g^{-1}) in urban soils obtained from Lahti green areas.

Compounds	No.													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Nap	6.56± 0.14	8.52± 0.86	48.42± 1.3	3.27± 0.61	14.23± 0.61	28.34± 0.05	68.92± 0.03	25.88± 0.36	4.18± 0.25	21.1± 0.24	4.18± 0.24	4.61± 0.35	2.69± 0.06	25.14± 0.48
2-MNa	7.9± 1.19	3.23± 0.33	17.24± 0.54	14.83± 0.23	20.75± 0.23	21.71± 0.09	51.61± 0.05	10.11± 0.02	8.14± 0.12	14.1± 0.03	5.23± 0.02	2.81± 0.27	ND	7.63± 0.1
Biph	ND	7.29± 0.58	33.54± 0.46	19.45± 0	3± 0.15	12.43± 0.03	53.68± 0.03	57.69± 0.21	ND	7.2± 0.07	3.91± 0.06	ND	ND	18.29± 0.22
Acy	ND	9.38± 0.35	6.31± 0.59	9.71± 0.26	1.07± 0.26	6.55± 0.09	48.42± 0.02	72.46± 0.08	ND	4.9± 0.23	ND	ND	ND	16.58± 0.17
Ace	1.01± 0.04	1.3± 0.76	21.96± 0.45	17.36± 0.19	ND	3.29± 0.04	49.74± 0.01	12.87± 0.01	ND		ND	ND	ND	21.36± 0.23
Flu	ND	10.24± 0.39	4.57± 2.18	12.59± 0.33	2.49± 0.38	4.45± 0.05	52.25± 0.02	42.47± 0.06	ND	8.4± 0.02	4.32± 0.02	ND	ND	11.72± 0.14
Phe	29.49± 3.23	0.1± 0.4	89.06± 0.97	22.18± 0.26	15.01± 0.07	21.47± 0.07	38.38± 0.04	58.48± 0.31	4.11± 0.12	8.7± 0.03	6.07± 0.03	2.55± 0.44	1.32± 1.37	14.81± 0.39
Ant	17.24± 1.63	11.16± 0.48	23.63± 1.12	10.95± 0.3	2.3± 1.78	4.04± 0.08	40.13± 0.19	36.02± 0.08	1.1± 0.05	4.9± 0.06	ND	ND	2.89± 0.08	9.47± 0.1
Fla	17.55± 0.75	8.41± 1.19	49.11± 2.12	20.32± 0.02	41.32± 0.87	40.52± 0.12	36.16± 0.1	44.73± 0.08	5.71± 0.19	36.3± 0.14	5.23± 0.18	1.29± 0.06	3.46± 0.2	20.55± 0.41
Pyr	26.13± 0.9	0.89± 0.25	61.36± 0.44	8.77± 2.35	41.44± 3.39	36.73± 0.1	59.45± 0.32	69.12± 0.16	6.29± 0.28	38.4± 0.02	4.98± 0.72	6.6± 0.29	8.03± 0.31	13.68± 0.17
BaA	ND	9.27± 1.11	62.86± 5.01	5.64± 0.06	19.25± 0.08	17.8± 0.05	36.78± 0.08	35.3± 0.03	ND	18.8± 0.18	2.93± 0.67	ND	6.03± 0.72	19.22± 0.35
Chr	ND	0.56± 2.46	45.76± 4.64	11.53± 0.85	28.72± 1.6	25.37± 0.03	42.62± 0.59	128.33± 1.49	ND	34.2± 0.15	4.67± 0.14	ND	6.75± 0.33	8.96± 0.07
BbF+BkF	3.75± 0.39	5.49± 0.85	60.47± 1.3	18.29± 0.88	51.53± 3.75	57.94± 0.04	111.29± 0.1	95.3± 0.08	3.58± 0.18	41.5± 0.12	ND	2.53± 0.35	3.47± 0.32	17.33± 0.87
BaP	ND	12.68± 0.32	39.27± 0.69	7.86± 0.09	18.68± 1.87	24.15± 0.02	43.66± 0.02	24.94± 0.02	ND	17.3± 0.04	ND	ND	ND	12.59± 0.37
DbA	53.54± 0.49	6.35± 1.69	18.43± 0.91	ND	5.21± 1.1	9.82± 0.03	57.03± 0.1	15.37± 0.11	ND	13.5± 0.06	ND	1.91± 0.17	5.98± 0.06	20.41± 0.84
BgP	ND	8.19± 0.95	39.64± 0.76	ND	16.35± 2.36	15± 0.02	41.29± 0.13	2.94± 0.02	4.22± 0.01	28.4± 0.03	ND	ND	ND	6.85± 0.38
∑16PAH	163.17	101.51	621.63	182.75	281.35	329.60	831.42	729.09	39.12	297.7	41.52	23.78	42.51	244.59

[a] Not detectable (for all observations falling below the LOD = 0.1053 µg*g^{-1}).

Table 4. Concentrations of polycyclic aromatic hydrocarbons (PAH) (ng*g-1) in urban soils obtained from Joensuu green areas.

Compounds	No.														
	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Nap	9.72± 0.41	4.18± 0.75	9.12± 1.14	11.65± 0.44	15.2± 0.05	5.67± 0.77	15.22± 0.8	22.52± 0.54	12.45± 0.52	28.56± 0.66	6.32± 0.09	14.57± 0.51	4.18± 0.02	3.04± 0.04	13.57± 1.38
2-MNa	ND	3.77± 0.15	3.97± 0.49	14.12± 0.4	17.77± 0.39	ND	21.8± 0.78	14.22± 0.52	7.32± 0.51	25.24± 0.25	ND	8.32± 0.53	3.77±0	ND	4.5± 0.35
Biph	7.36± 0.07	5.13± 0.05	ND	3.55± 0.69	4.39± 0.05	4.32± 0.63	4.52± 0.7	5.81± 0.57	18.59± 0.54	32.37± 1.71	ND	12.49± 0.06	5.13± 0.01	ND	ND
Acy	8.21± 0.53	2.79± 0.6	ND	8.97± 0.5	9.88± 0.6	ND	25.23± 0.87	25.04± 0.59	9.28± 0.57	33.98± 2.7	ND	10.41± 0.01	2.79± 0	ND	ND
Ace	ND	3.91± 0.94	ND	1.38± 0.94	ND	ND	2.44± 0.59	1.76± 0.63	10.39± 0.61	34.89± 0.15	ND	9.37± 0.02	ND	ND	ND
Flu	ND	4.32± 0.69	3.23± 0.83	10.28± 0.85	3.21± 0.3	ND	11.3± 0.98	4.33± 0.69	14.55± 0.66	44.7± 1.51	ND	11.45± 0.23	4.32± 2.35	ND	1.33± 0.14
Pyr	10.28± 0.53	6.07± 0.55	40.65± 0.95	23.1± 0.44	11.62± 4.53	6.21± 0.58	44.02± 0.52	28.62± 0.53	6.21± 0.51	90.72± 0.84	38.65± 2.18	7.28± 0.01	6.07± 0.06	ND	14.9± 0.56
Ant	3.69± 0.03	ND	37.37± 1.16	10.16± 1.15	4.65± 9.56	ND	17.75± 0.34	14.27± 0.56	11.36± 0.53	3.06± 0.03	40.24± 0.55	13.53± 0.05	2.86± 0.85	ND	19.55± 0.17
Fla	11.17± 0.24	5.23± 0.55	10.74± 0.17	77.84± 1.85	23.82± 2.16	ND	184.42± 0.88	135.05± 0.69	8.27± 0.67	66.45± 0.36	8.75± 0.59	16.65± 0.34	5.23± 0.88	ND	13.44± 0.98
Pyr	6.45± 0.75	3.42± 0.3	20.43± 0.12	132.37± 1.1	27.71± 1.26	14.89± 0.94	158.48± 0.61	118.47± 0.72	13.42± 0.67	72.2±1	13.43± 1.15	16.25± 0.11	ND	3.26± 0.04	21.55± 0.54
BaA	8.33± 0.08	4.98± 0.75	5.63± 0.5	33.59± 1.75	8.48± 2.22	ND	81.19± 0.78	69.64± 0.49	16.53± 0.47	196.75± 0.14	1.99± 0.35	15.61± 0.03	3.55± 0.56	ND	ND
Chr	9.62± 0.82	ND	ND	68.3± 1.25	14.68± 0.73	ND	87.98± 0.61	71.55± 0.39	5.18± 0.39	51.42± 0.15	ND	5.21± 0.15	4.98± 0.07	ND	2.34± 0.65
BbF+BkF	7.58± 0.25	4.67± 0.69	ND	124.67± 0.69	32.1± 2.54	ND	168.7± 0.38	176.39± 0.67	17.47± 0.65	193.06± 2.77	ND	17.69± 0.49	1.93± 0.38	ND	ND±0
BaP	ND	6.12± 0.94	ND	40.54± 0.94	26.73± 1.38	3.45± 0.8	70.04± 0.08	52.75± 0.64	4.16± 0.63	93.33± 1.69	ND	24.17± 0.12	4.67± 0.33	ND	ND
DbA	12.74± 1.76	ND	17.32± 0.44	9.31±1	5.59± 0.86	ND	15.12± 0.29	16.32± 0.56	15.51± 0.54	135.88± 0.84	19.26± 1.48	18.73± 0.06	ND	ND	40.56± 1.13
BgP	9.72± 0.41	4.29± 0.85	ND	81.92 ±0.85	23.77± 6.74	ND	33.98± 0.36	36.99± 0.69	17.08± 0.66	71.34± 4.35	ND	3.13± 0.01	1.29± 0.3	8.08± 0.85	ND
∑16PAH	95.15	58.88	148.46	651.75	229.6	34.54	942.15	793.73	187.77	1173.95	128.64	204.86	50.77	14.38	131.74

Not detectable (for all observations falling below the LOD = 0.1053 μg*g^{-1})

3.3 Ecotoxicity of soils sampled in green areas in Lahti and Joensuu

Ecotoxicity bioassays are essential complements to chemical analyses for evaluating the impact of pollutants on living species [41]. In our study, a bioassay based on infusoria was employed to estimate the integral toxicity of water-soluble components of soils [42–45]. As shown in Figure 2, three samples—No. 2, 11, and 14 (Lahti), and No. 15, 19, and 28 (Joensuu)—were non-toxic to *P. caudatum*. The toxicity of other undiluted elutriates exceeded 10%, necessitating a series of additional dilutions and the calculation of LID10. To achieve the non-toxic level (10%) for samples from Lahti, higher dilutions were required compared to samples from Joensuu. Soil samples from Joensuu parks were 1.2 times less toxic towards paramecia, with an LID10 range of 6–34, than those from Lahti parks, which had an LID10 range of 7–40.

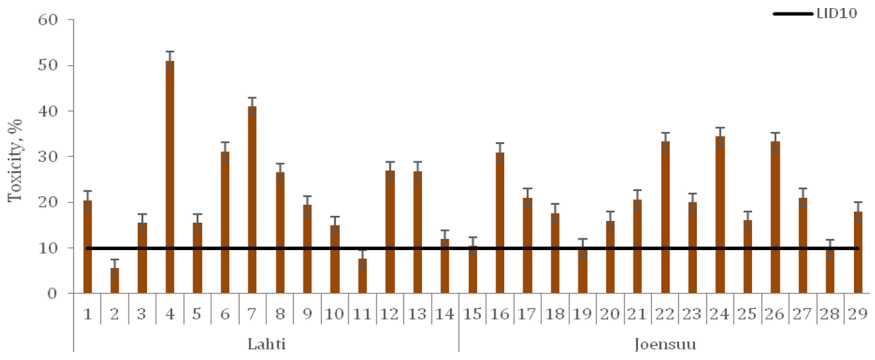

Fig. 2. Ecotoxicity of undiluted samples (liquid elutrites) obtained from parks and green zones of Lahti and Joensuu assessed by means of *P. caudatum.* Samples with toxicity exceeding 10% (black line) were subjected to series dilution and LID10 estimation.

The high toxicity of the initial samples (undiluted elutriates) may be attributed not only to the high content of metals in the soil, such as Cu (No. 4) and PAHs (No. 3), but also to the cumulative effect of these factors. Similarly, the toxicity of the samples is due to high contents of Cd (No. 13, 24, 27, 29), as well as Zn (No. 25) and/or PAHs (No. 5, 6, 7, 10, 18, 21, 22, 26). The toxicity of samples No. 8, 9, 12, 16, 17, 20, 23 is likely due to the presence of other toxic substances or the sensitivity of the infusoria themselves. Samples No. 1, 2, 11, 14, 15, 19, 28, which were non-toxic, likely contained lower concentrations of pollutants or none at all.

The correlation coefficients characterizing the relationship between the content of metals in the soil and toxicity towards *P. caudatum* showed that there is a moderate correlation only with the content of Cu in the soil ($r = 0.63$). In other cases, the influence of individual metals on the survivability of the test organism was not reliably established. The LID10 results correlated with the overall level of contamination by metals (Zc) ($r = 0.75$), but there was no correlation with ∑16PAHs ($r = 0.39$). This is likely because metals in the aquatic environment are in dissolved and adsorbed states (unlike PAHs) and pose a potential threat to aquatic organisms. Since the bioassay involves preparing an aqueous elutriate of soil, metals can disrupt the integrity of physiological and biochemical processes, causing significant changes in metabolic reactions in hydrobionts [46–48].

4 Conclusion

It can be concluded that urban park soils in two mid-sized Finnish cities, Lahti and Joensuu, range from low contamination to moderate with PAHs and permissible to high contamination with metals, mainly Cd. As the metals' compounds are water-soluble, their presence significantly contributes to the soils' ecotoxicity towards *P. caudatum*.

Acknowledgement

The work is carried out in accordance with the Strategic Academic Leadership Program "Priority 2030" of the Kazan Federal University of the Government of the Russian Federation. We are grateful to Kone Foundation (Finland) for funding the "LesRus" project that supported soil sampling and experimental planning. We thank the project coordinator Ph. D. Aki Sinkkonen.

References

1. Report on Carcinogens, Twelfth Edition (2011). U.S. Department of Health and Human Services Public Health Service National Toxicology Program, 507, (2009)
2. Y.F. Jiang, X.T. Wang, F. Wang, Y. Jia, M.H. Wu, G.Y Sheng, J.M. Fu. Chemosphere, **75**, 1112-1118 (2009)
3. USEPA: Toxic Release Inventory Public Data Release (2000)
4. L. Madrid, E. Díaz-Barrientos, F. Madrid. Chemosphere, **49**, 1301-1308 (2002)
5. L. Tang, X.Y. Tang, Y.G Zhu, M.H. Zheng, Q.L Miao. Environ. Int. **31**, 822-828 (2005)
6. W.E.H Blum. Rev. Environ. Sci. Biotechnol. **4**, 75-79 (2005)
7. T. Sattler, P. Duelli, M.K. Obrist, R. Arlettaz, M. Moretti. Landsc. Ecol. **25**, 941-954 (2010)
8. L. Santorufo, C.A.M. Van Gestel, G. Maisto, Chemosphere, **88**, 418-425 (2012)

9. E.S. Shuklina, N.N. Voropaj, A.A. Cherkashina, Dinamika i vzaimodejstvie geosfer zemli (Tomsk), **2**, 215–216 (2021)
10. World Health Organization (WHO): Permissible limits of heavy metals in soil and plants (Geneva, Switzerland) (1999)
11. FAO: Government decree on the assessment of soil contamination and remediation needs. Ministry of the Environment, Finland, Government Decree 214/2007 on the Assessment of Soil Contamination and Remediation Needs (2007)
12. G. Suresh, V. Ramasamy, V. Meenakshisundaram, R. Venkatachalapathy, V.Ponnusamy, Appl. Radiat. Isot. **69**, 1466-1474 (2011)
13. D.L. Tomlinson, J.G.Wilson, C.R.Harris, D.W. Jeffrey. Helgoländer Meeres. 33, 566-575 (1980).
14. Yu. Saet, B.Revich, E.Yanin, Geohimiya okruzhayushchej sredy, 335 (1990)
15. MU 2.1.7.730-99 Pochva, ochistka naselennyh mest, bytovye i promyshlennye othody, sanitarnaya ohrana pochvy, (1999)
16. Y. Lu, Z. Gong, G. Zhang, W. Burghardt, Geoderma, **115**, 101-111 (2003)
17. A. Kamalova, P. Galitskaya, A. Gordeev, A. Khamieva, P. Kuryntseva, International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM. **23**, 89-95 (2023)
18. B. Maliszewska-Kordybach, Appl. Geochemistry. **1**, 121-127 (1996)
19. E. Morillo, A. S. Romero, C. Maqueda, L. Madrid, F. Ajmone-Marsan, H. Grcman, C. M. Davidson, A. S. Hursthouse, J. Villaverde, Journal of Environ. Mon. **9**, 1001-1008 (2007)
20. P. Kuryntseva, P. Galitskaya, S. Selivanovskaya, Waste Manag. **58**, 90-97 (2016)
21. U.S. Environmental Protection Agency: Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. 486 (2002)
22. G. Maisto, S.Manzo, F. De Nicola, R Carotenuto, A.Rocco, A.Alfani. J. Environ. Monit. **13**, 3049-3056 (2011)
23. M.A.P. Davis, Ni. S Shokouhian. Chemosphere, 44, 997-1009 (2001)
24. N. O. Eddy, S. A. Odoemelem, A. Mbaba, Agric. Food Chem. 5, 1349-1365 (2006)
25. B.B. Dagne, T. Endale. African J. Agric. Res. **14**, 78-91 (2019)
26. E.M. Nikiforova, N.S.Kasimov, N.E. Kosheleva, I. V.Timofeev. Environ. Geochem. Health, **44**, 1697-1711 (2022)
27. A. Kamalova, A. Gordeev, P. Galitskaya, S. Selivanovskaya. Smart and Sustainable Urban Ecosystems: Challenges and Solutions (SSC-2022), 43-65 (2023)
28. G. Navarrete-Rodríguez, M.D.R Castañeda-Chávez, F. Lango-Reynoso. Int. J. Environ. Res. Public Health, **17**, 963 (2020)
29. L. Hakanson.Water Res. **14**, 975-1001 (1980)
30. G.D. Martin, R. George, P. Shaiju, K.R. Muraleedharan, S.M. Nair, N. Chandramohanakumar. Sci. World J. 2012, 17 (2012)
31. M.H. Rezaie-Boroon, V. Toress, S. Diaz, T. Lazzaretto, M. Tsang, , D.D. Deheyn. J. Environ. Prot. (Irvine,. Calif), **04**, 12-25 (2013)
32. T.V. Minnikova, T.V. Denisova, S.S. Mandzhieva, S.I. Kolesnikov, T.M. Minkina, V.A Chaplygin, M.V. Burachevskaya, S.N. Sushkova, T.V. Bauer, J. Geochemical Explor. **174**, 70-78 (2017)

33. N.S. Kasimov, D.V. Vlasov. Vestn. Mosk. Univ. Seriya 5 Geogr. 2018-January, 14 (2018)
34. J. Yan, L. Wang, P.P. Fu, H. Yu, Mutat. Res. Genet. Toxicol. Environ. Mutagen. **557**, 99-108 (2004)
35. T. Goydina, Lahti - the green capital of Europe, https://euro-pulse.ru/eurotrend/gorod-stoproczentnoj-chistoty-kak-lahti-stal-zelenoj-stoliczej-evropy/
36. D. Crnkovic, M. Ristic, A. Jovanovic, D. Antonovic. Environ. Monit. Assess. **125**, 75-83 (2007)
37. A. Parajuli, M. Grönroos, S. Kauppi, T. Płociniczak, M.I. Roslund, P. Galitskaya, O.H. Laitinen, H. Hyoty, A. Jumpponen, R Strömmer, M. Romantschuk, N. Hui, A. Sinkkonen. PLoS One, 12, 1-18 (2017)
38. V. Mantylahti, P. Laakso. Food Sci. Finl. **11**, 285-300 (2002)
39. I.P. Adejoh. Adv. Appl. Sci. Res. **2**, 20-27 (2016)
40. L.S. Bjelic, D.N. Markic, P. Ilić, Z.U.R. Farooqi, Polish J. Environ. Stud. **31**, 595-608 (2022)
41. J. Xu, X Ke, P.H. Krogh,Y. Wang, Y.M. Luo, J. Song, Insect Sci. **16**, 57-63 (2009)
42. P. Kuryntseva, P. Galitskaya, S. Selivanovskaya, Water Environ. J. **36**, 270-281 (2022)
43. J.V. Rao,V.G. Gunda, K..Srikanth, S.K. Arepalli, Toxicol. Environ. Chem. **89**, 307-317 (2007)
44. R.M. Potekhina, E.I. Semenov, I. V. Medvedeva, K.A. Osyanin, N.M. Aleksandrova, E.A. Shuralev, Bionanoscience, **10**, 799-806 (2020)
45. N. Stepanova, V.Z. Latypova, M.V. Trushin, Am. J. Agric. Environ. Sci. **11**, 490-494 (2011)
46. K.H.H. Aziz, F.S. Mustafa, K.M. Omer, S. Hama, R.F. Hamarawf, K.O. Rahman, RSC Adv. **13**, 17595-17610 (2023)
47. S.S. Sonone, S. Jadhav, M.S. Sankhla, R. Kumar, Lett. Appl. NanoBioScience. **10**, 2148-2166 (2021)
48. S.C. Deb, T. Fukushima, Int. J. Environ. Stud. **56**, 385-417 (1999).
49. Supplement materials, https://cloud.mail.ru/public/Xc1Y/nnRQhQUHH