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Content of trace elements, ^{137}Cs and ^{40}K in bioindicators and soils from Kyiv (Ukraine)

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Abstract
In leaves of *Tilia cordata* Mill., and soils from Kyiv localities with different levels of anthropogenic impact, total concentrations of Ni, Cr, Cu, Pb, Cd, and Hg were determined using mass-spectrometry with inductively cupled plasma, and activities of ^{137}Cs and ^{40}K were measured with gamma-spectrometry. Also in bodies of *Apis mellifera* Linnaeus 23 mineral elements (including toxic and heavy metals) were determined with mass-spectrometry. Even taking into account only six heavy metals, it can be concluded that all urboecotopes undergo a complex technogenic load. The total hazard ratios in soils (reflecting the multiplicity of exceedance of the maximum permissible levels) were in the intervals: in parks - 21.24 to 83.91; in areas adjacent to residential – from 45.11 to 63.22; along roads with middle traffic from 34.59 to 54.32; along highways with intensive traffic - from 48.39 to 94.34; at industrial zone – 120.12.

Keywords: bioindication, *Tilia cordata, Apis mellifera,* heavy metals

Introduction

At present, a worsening of air quality, an augmentation of the levels of toxic emissions and industrial wastes, an increase in transport loads requires biomonitoring of the urban environment. It is well known that bio-indication, as a branch of environmental monitoring, uses a wide range of biological objects. Plants, animals, mushrooms are considered as reliable informative qualitative and respectively qualitative indicators of environmental pollution by heavy metals, and radionuclides in particular [1-11].

Among a number of environmental pollutants, heavy metals are predominant; including priority is mercury, lead, copper, nickel, cadmium, etc. Nowadays they share a high rate of accumulation in the environment. Geochemical studies indicate that under the influence of technogenic contamination in soils the content of moving forms of heavy metals increases, but the buffer capacity of such soils, respectively, decreases. Mobile forms of chemical elements determining their migratory capacity in the food chain soil-plant-animal-man, which largely depends on the physical-chemical characteristics of soils [10-12].

The city of Kyiv (The capital of Ukraine) is located in the north of Ukraine, on the border of Polissya and the forest-steppe zone. The area of Kyiv within the administrative boundaries reaches 836 km^2. From the north to the south, the city stretches for 42.1 km, from west to east – 41.9 km, its geographical coordinates are: north latitude - 50°26'; eastern longitude - 30°34', average altitude is 105 m. The city's built-up land is 364.0 km^2, and 115.0 km^2 of which are under residential and public buildings. A significant amount of land occupied by industrial facilities - 56.0 km^2, objects of transport and communication – 22.0 km^2. Most of the city lies on the high right bank of the Dnipro - the Kyiv plateau cut by a thick net of ravines (Babyn, Khreshchatyi, Smorodinskyi, and others). Characteristic forms of the relief of the right bank - mountains-remnants. The smallest part is on the lower left bank of the Dnipro. The lower parts of the city of Kyiv correspond to the water level in the Dnipro and make up about 92 m altitude. On the territory of the city there are 9 rivers - the Dnipro, Syrets', Hlybochytsya, Skomorokh, Darnytsya, Lybid', Vita, Sovka, Nyvka. The largest lakes are Vyrlytsya, Radunka, and Tel'byn [13].

The city of Kyiv is the most important railways, highways and airways of Ukraine 84.4% of the total emissions of polluting, harmful to human health, make mobile sources - motor vehicles, mainly personal cars. According to data of the Central Geophysical Observatory of the Ministry of Emergencies, the already high concentration of nitrogen dioxide in the air of

Kyiv, exceeding the norm more than twice, in summer can increase five to six times due to the large congestion of cars and for certain weather conditions. Among the industries, the largest stationary pollutants in the air remain energy and manufacturing industries. In general, according to state statistical sources, during 2015, the city's atmosphere totaled 171 thousand tons of pollutants from stationary and mobile sources of pollution [14].

The aim of present study was to evaluate the state of technogenic pollution of Kyiv for the analysis of heavy metals contents and radionuclides activity in leaves of *Tilia cordata* Mill. bodies of *Apis mellifera* L., and in soils from ecotops with different antropogenic loads.

Materials and Methods

The content of heavy metals (Cd, Cr, Cu, Hg, Ni, Pb) examined in 2014 and 2015 in soils (average sample of 0-5 cm) and leaves of *T. cordata* (≥30 intact, developed leaves from each of three trees from one location) from Kyiv locations (within 10 administrative district with different levels of contamination, 14 on the right and 7 on the left bank of Dnipro river, Table 1, Fig. 1) were measured using inductively coupled plasma mass-spectrometry (ICP-MS) (Analyzer Element-2, Germany) according approach described by O.M. Ponomarenko *et al*. (2008) [15]. The reagent and/or their solutions used, namely alkaline meltable reagents – Na_2O_2, $LiBO_2$ (Analytically pure), and concentrated acids HF, HCl, HNO_3, H_2SO_4, H_3PO_4 (highly pure) were additionally cleaned using Subboiling system. Water having 18.2 MΩ/cm resistance was obtained using Direct-03 system (Millipore). Samples were dissolved using an Ethos microwave laboratory oven (Milestone, Italy). The working frequency of a microwave irradiation was equal to 2450 MHz and maximal output power – to 1600 W. Indium isotope, ^{115}In, was used as an internal standard, while normal samples of essexite gabro rock and gold ore tailings were used as external standards.

During the selection of honey bees were guided by the scheme of selection of leaves of *T. cordata*. In dried *A. mellifera* bodies the content of 23 mineral elements were measured with mass-spectrometry (ICP-MS).

The park Feofaniya, located on the southwestern border of Kyiv, we previously selected as a locality with a minimum anthropogenic pollution (reference location). Since 1972, the forested area of the experimental forestry Feofaniya has received the status of a protected area as the park-monument of landscape art [16]. At the present time, the park belongs to the 3rd category of the IUCN - "Natural Monument or Feature", and plays an important role in the preservation and reproduction of biodiversity (https://www.protectedplanet.net/feofaniya-state-park-monument-of-orchard-park-art). As the most contaminated ecotope was chosen a locality on the territory of the former plant “Radical”. In present study the classification of ecotopes according to the EUNIS [17] was used (Table 1).

^{137}Cs and ^{40}K activity in leaves of *T. cordata*, bodies of *A. mellifera* have been studied using gamma-spectrometry (Ge-detector Canberra GLX 4019). For analysis samples of soils (average sample from 0-5 cm of upper soil layer), leaves (up to 30), bees bodies (20) dried at 80 °C, then reduced to fine-dispersed powder and additionally dried up at 105 °C during 24 hours, then placed in plastic bags. The counting time was 6-36 hours. Counting errors for the measurements of ^{137}Cs were usually lower than 5%. The statistical analysis was carried out using Microsoft Excel 2013 and SPSS Statistics for Windows 22.0 software packages (IBM Corp., 2013).

Results and Discussion

Our previous studies have demonstrated the positive correlation between the value of index of stress (reverse vegetation index), measured with spectrophotometry in leaves of bioindicator species *Tilia cordata* Mill., and *Taraxacum officinale* Webb., and traffic intensity in the city of Kyiv (Ukraine). The index of stress was defined on the base of measurements as: IS = R1 / R2, where the spectral reflection coefficients in green R1 (551.9 nm), and near infrared – R2 (802.0 nm) range of spectrum [18, 19, 20, 21, 22, 23].

A study on morphometric parameters of *T. cordata* leaf plates from Kyiv ecotops with different levels of technogenic loads has shown that only some parameters (In particular, leaf area, petiole length and coefficients of variation) reliably reflect the degree of environmental contamination. And, at the same time, it should be noted that for the purpose of bioindication, it is expedient the using of the morphometric method only in combination with other analytical methods. It is known that urban soils are very complex for biotesting objects, due to the diversity and abundance of pollutants that are present in them. The toxicity of heavy metals for biota objects is related to their biological activity and availability, stability of their compounds in the environment (Since, unlike organic matter, metal ions weakly transformed and, having fallen in the biogeochemical cycle, remain in it) and the ability, even in low concentrations, to cause significant negative effects [10, 11, 24].

For the processes of mobilization and plant uptake of trace elements, in particular, the effect of the microbial activity in the rhizosphere is important, since mutualistic symbionts, like mycorrhizal fungi, can significantly control the accumulation or removal of trace elements from host plants [25, 26, 27, 28].

Publications of recent years are devoted to studies on the accumulation of heavy metals by leaves of woody plants in urbanized territories [8, 24, 29, 30, 31, 32, 33, 34, 35].

The studies on the distribution of heavy metals (lead, cadmium, mercury, copper, chromium and nickel) carried out by methods of atomic absorption mass spectrometry showed complex and uneven pollution of soil contamination in Kyiv (Table 2). At present, the maximum permissible concentrations of heavy metals in soils are not sufficiently developed, the choice of background reference content is important in the processing of ecological and geochemical information. However, in conditions of the current level of technogenic contamination of urban territories with a complex of identified and uncertain factors, the choice of reference locality is rather subjective. In particular, soil samples from our selected reference localization Park Feofaniya contained elevated levels of copper and chromium (Table 2, 3).

In order to assess the degree of risk of heavy metals, a hazard ratio (HR) was used - the ratio between the concentration of a certain element in the sample and its permissible concentration [36]. Also, to estimate the rate of accumulation of metals, a bioaccumulation factor (BAF) was also calculated. It is equal to the ratio of the element content in the biological object to its content in the soil at the sampling site.

Parks (Ecotopes X11 and X23)

Among the studied parks the highest level of contamination with Ni observed in soil samples from Mariins’kyi Park (34 mg/kg dry mass), prevalence on permissible levels, or hazard ratio (HR), amounted to 8, Cr and Cu – in soils from Park Feofaniya, accordingly - 80 mg/kg dm (HR – 13.33) and 180 mg/kg dm (HR – 60) (Table 2-4). The highest level of Pb in soils of park ecotopes was fixed in Pushkin Park - up to 60 mg/kg dm (HR - 3). Levels of Cd in soil samples were within 0.24 mg/kg dm in Park Dubky (HR – 0.12), and 0.12 mg/kg dm in Mariins'kyi Park (HR - 0.06). Levels of Hg in soil samples were from 0.04 mg/kg dm in Pushkin Park (HR – 0.018) to 0.03 mg/kg dm (HR - 0.014) in all other studied parks. At the same time, the highest levels of metals determined in leaf biomass did not coincide with the levels in soil samples. Evidently, the elevated content of some heavy metals in the leaves of *T. cordata* from different locations reflects the activity of migration processes of mobile forms of heavy metals in soils and the capacity of plants to uptake water-soluble forms of mineral elements. It is also important to note that in this study we do not consider separately the contribution of air pollutants. The highest level of Ni was detected in leaves of *T. cordata* from Park Dubky- 8.5 mg/kg dm, for these samples a bio-accumulation factor, BAF, was 1.19) (Table 4). The highest level of Cr was determined in leaves from Pushkin Park – up to 30 mg/kg dm (HR-5). In all other parks BAFs for Cr were<1 (Table 4). Highest level of Cu in *T. cordata* leaves were in Mariins'ky Park – 48 mg/kg dm (HR-16), in all parks BAFs for Cu also were <1. A highest level of Pb was in leaves from Park Dubky – 3.8 mg/kg dm (HR – 0.19). Levels of Cd in leaves were within 0.08 mg/kg dm (Park Dubky) – 0.03 (Park Feofaniya and Pushkin Park), BAFs in all cases were <1. Content of Hg in all leaves samples not exceeded 0.03 mg/kg dm (HR - 0.014).

A maximal total hazard ratio (Σ HR) of heavy metals was in soils of Park Feofaniya – 83.91 and in leaves from Mariins'kyi Park – 18.01. Based on the total HRs (Table 3, 5), park ecotops by degree of pollution can be represented in the form of the following sequences:

For soils: Park Dubky < Mariins'kyi Park < Pushkin Park < Park Nyvky < Park Feofaniya

For T. cordata leaves: Park Dubky < Pushkin Park < < Park Nyvky < Park Feofaniya < Mariins'kyi Park. It must be noted that the index of stress (IS) for this ecotope, measured in our previous investigation were in the range from 0.132 to 0.216 (The mean value – 0.182), 2016) [10].

Areas adjacent to residential buildings, distance from the road ≤ 20m (ecotopes J4.6)

For these ecotopes, the highest content in the soils of Cu (110 mg/kg dm, HR – 36.67), Ni (60 mg/kg dm, HR – 15), and Cr (52 mg/kg dm, HR – 8.67) was found on the Holosiivskyi Ave. The highest levels of Pb, Cd and Hg were detected in soils in the left bank of the city – on Harkivs'ke Ave, respectively - 80 mg/kg dm (HR – 4), 0.16 mg/kg dm (HR-0.08), and 0.06 (HR – 0.03). The same content of Hg found in soils from Mytropolyta A. Sheptyts'kogo Str. However, as in the case of park ecotops, the detected maximum levels of these metals in the leaves of lindens did not always coincide with the high levels of these elements in the soils of the corresponding habitats. Thus, the highest content of Ni and Hg in the leaves of *T. cordata* was found on the Harkivs'ke Ave (correspondingly 3.8 and 0.06 mg/kg dm), Cr and Pb on the Holosiivs'kyi Ave (respectively 4.1 and 6 mg/kg dm), Cu and Cd – on Mytropolyta A. Sheptyts'kogo Str. (respectively, 51 and 0.08 mg/kg dm). It need to note that in the case of Ni, BAFs were in the range from 0.05 to 0.12; for Cr – 0.06 to 0.1, for Cu – from 0.16 to 0.65, for Pb – from 0.04 to 0.11, for Cd from 0.38 to 0.57, and for Hg from 0.67 to 1.25 (on Mytropolyta A. Sheptyts'kogo Str.).

A maximal total hazard ratio (Σ HR) of heavy metals was in soils on Golosiivs'kyi Ave – 63.22 and in leaves from Mytropolyta A. Sheptyts'kogo Str. – 18.61. Based on the total HRs, these ecotops by degree of pollution can be represented next sequences:

For soils: Harkivs'ke Ave < Mytropolyta A. Sheptyts'kogo Str. < Holosiivs'kyi Ave;

For T. cordata leaves: < Holosiivs'kyi Ave < Harkivs'ke Ave < Mytropolyta A. Sheptyts'kogo Str.

The indexes of stress (IS) for this ecotope were higher than in parks (from 0.137 to 0.239, the mean value – 0.192).

Along the roads with middle traffic (ecotopes J4.2)

The highest content of Ni in soil samples was on Metrologichna Str. – 54 (HR - 13.5). Maximal Cr levels (60 mg/kg dm, HR – 10) determined in soils on Metrologichna and Magnitigors'ka streets. The highest content of Cu was found in soils from Dragomanova Str. – 85 (HR – 28.33). Besides only one locality – Verbyts'kogo Str., where Pb content in soil was 62 mg/kg dm, in all others locations this value was higher – up to 80 mg/kg dm (HR – 4). The highest levels of Hg – 0.08 mg/kg dm (HR – 0.04) were on Metrologichna, Magnitogors'ka and Dragomanova streets. For this group of ecotopes, there were more cases of compliance with the maximum levels of accumulation of metals by leaves with their high content in soils from the location. The highest level of Ni in leaves was found on Dragomanova Str. – 12.4 mg/kg dm (HR – 3.1). In leaves the maximum contents of Cd and Cr were found on Metrologichna Str. – 0.82 mg/kg dm (HR -0.41), and 5.1 mg/kg dm The highest level of Cu in leaves was found on the street Verhniy Val, and Pb – 5.1 mg/kg dm (Hr – 0.26) on Magnitogors'ka Str. The highest level of Hg – 0.76 (HR – 0.35) was found on Metrologichna Str., for this location it must be noted extremely high BAF – 9.5. Other coefficients of bioaccumulation in leaves were in the range of 0.07 (Magnitogors'ka) and 0.5 (Dragomanova Str.) for Ni; for Cr – 0.05 (Magnitogors'ka Str.) and 0.1 (Verhniy Val Str.); for Cu – 0.28 (Verbyts'kogo Str.) and 1.11 (Verhniy Val Str.); for Pb – 0.03 (Verbyts'kogo Str.) and 0.07 (Dragomanova Str.); for Cd – 0.29 (Verhniy Val Str.) and 5.3 (Metrologichna Str.), and for Hg – 0.57 (Verbyts'kogo Str.) and 9.5 (Metrologichna Str.). The maximum total hazard ratios for this type of ecotopes were observed on Metrologichna Str. – 54.32 (soil) and Verhniy Val Str. (leaves) - 21.69.

Based on the total HRs, these ecotops by degree of pollution can be represented next sequences:

For soils: Verhniy Val Str. < Dragomanova Str. < Magnitogors'ka Str. < Verbyts'kogo Str. < Metrologichna Str.

For T. cordata leaves: Verbyts'kogo Str. < Dragomanova Str < Magnitogors'ka Str. < Metrologichna Str. < Verhniy Val Str.

The index of stress for these ecotope were from 0.138 to 0.233 (the mean value – 0.198).

Along the highways with intensive traffic (ecotopes J.4.2)

It should be noted that near the roads with intensive traffic, the strongest lesions of the leaves were noted – numerous necrotic spots on leaves, fungal damage, early shrinkage. The highest content of Cu in soil samples was determined on the Nauky Ave – 210 mg/kg dm (HR- 70). A maximal value for Pb was found in soil from the intersection of streets Khreschatyk and Prorizna (in the heart of the city) – 410 mg/kg dm (HR-20.5). The highest contents of Cr, Ni, Cd and Hg were found on the Peremogy Ave (near a gas station) - 240 mg/kg dm (HR - 40), 51 mg/kg dm (HR - 12.65), 0.16

mg/kg dm (HR-0.08), and 0.08 mg/kg dm (HR – 0.036), respectively.

But maximal values of Ni, Cr in *T. cordata* leaves were found on Naberezhno-Khreshatyts'ka Str. – 6.6 mg/kg dm (HR - 1.65) and 5.1 mg/kg dm (HR – 0.85), Cu, Cd and Hg – on Peremogy Ave – 50 mg/kg dm (HR – 16.67), 0.1 mg/kg dm (HR-0,05) and 0.08 mg/kg dm (HR – 0.036), respectively, and Pb - 30 mg/kg dm on Nauky Ave (HR-1.5). Bio-accumulation factors for Ni in leaves were in the range of 0.05 (Grushevs'kogo Str.) up to 0.12 (Naberezhno-Khreshatyts'ka Str), for Cr - within 0.02 (Peremogy Ave) and 0.13 (Grushevs'kogo Str), for Cu – within 0.06 (Nauky Ave) and 0.14 (Grushevs'kogo Str.), for Pb – within 0.02 (Khreschatyk/Prorizna) and 0.5 (Nauky Ave), for Cd – within 0.29 (Druzhby Narodiv Blvd) and 0.63 (Peremogy Ave), for Hg – within 0.57 (Harkivs'ke Ave) and 1.5 (Druzhby Narodiv Blvd). The calculation of the total hazard ratios in this group of ecotopes showed that the maximum coefficient - 94.32 is fixed on the Nauky Ave, and the minimum - 48.34 - on Druzhby Narodiv Blvd (Table 3). It should be noted that near the roads with intensive traffic, the strongest lesions of the leaves were noted - necrotic spots, fungal damage, early shrinkage. Glibovyts'ka (2014) [31] also cites similar phenomena. Based on the total HRs, these ecotops by degree of pollution represent next sequences:

For soil: Druzhby Narodiv Blvd < Harkivs'ke Ave < Naberezhno-Khreschatyts'ka Str. < Grushevs'kogo Str.< Hreschatyk/Prorizna streets< Peremogy Ave < Nauky Ave

For T.cordata leaves: Hreschatyk/Prorizna streets < Nauky Ave < Grushevs'kogo Str.< Naberezhno-Khreschatyts'ka Str. < Harkivs'ke Ave <Druzhby Narodiv Blvd < Peremogy Ave.

The index of stress for these ecotope were from 0.187 to 0.240 (the mean value – 0.217).

Constructed, industrial and other artificial habitats (ecotope J6.52)

The Factory Radical is one of the dangerous contaminated with heavy metals territories in the city of Kyiv. It was chosen as extreme industrial pollution location. Because of *T. cordata* trees are absent at this area, it wasn't possible to collect leaves samples. Despite the fact that more than 18 years have passed since its closure, and that certain measures have been taken for cleaning its territory, soil samples contain dangerous levels of heavy metals (Table 2, 3)– Cu – 240 mg/kg dm (HR-70), Cr – 110 mg/kg dm (HR-18), Ni -64 mg/kg dm (HR -16), Cd -0.24 mg/kg dm (HR-0.12), Pb - 210 mg/kg dm (HR – 10.5), Hg -1.1 mg/kg dm (HR – 0.5). For obvious reasons, the total hazard ratio in this ecotope reached its maximum value – 120.12.

The obtained data testify to the complex nature of technogenic pollution of all ecotopes of Kyiv, as evidenced by the ranges of hazard ratios (Table 5). Actually, park areas can not be considered a reference (etalon) because they have a rather high level of contamination with heavy metals. Even with only 6 elements studied, it can be concluded that all urban ecotopes are under heavy technogenic loading, the total exceedance of the maximum permissible concentrations in ecotopes was from 6.53 to 21.69 (leaves) and 21.24 to 120.21 (soils). The critical level of man-made and anthropogenic pollution in the city of Kyiv causes a catastrophic condition of street green plantations (chlorosis and necrosis of leaves, defoliation of the crown in summer, drying of branches and trees), which requires urgent measures for the improvement of tree stands, planting of trees of persistent breeds, increasing areas of green areas, etc.

The accident at the Chernobyl nuclear power plant in 1986, which led to radioactive contamination of vast territories not only in Ukraine, but also in neighboring countries, dictates the need for long-term radioecological monitoring of biota objects. In samples of leaves from the parks of Kyiv, the activity of radiocesium was usually below the detection limit (BDL), ^{40}K activity was in the range of 49 to 104 Bq/kg dry mass. The level of soil contamination in park areas was also negligible; activity of radiocaesium was in the range from 17 to 87 Bq/ kg dm. (Table 6).

For samples of leaf biomass, selected on areas adjacent to residential buildings, in most cases, the level of radiocaesium was BDL, and the level of soil contamination was 11 - 81 Bq/kg dm. Along the roads with middle traffic the highest activity of ^{137}Cs (300 Bq/kg dm) was found on Magnitogors'ka Str., and minimal – 15 Bq/kg dm at Metrologichna Str. At the same time, 50% of *T. cordata* leaves at these ecotops have radiocesium activity below detection limit and ^{40}K within 17 – 70 Bq/kg dm. In leaves samples collected along the highways with intensive traffic, radiocesium activity was within BDL and 18 Bq/kg dm., and ^{40}K – 68 and 148 Bq/kg dm, and in soils of these ecotops activity of ^{137}Cs was within 16 and 157 Bq/kg dm, and ^{40}K – 39 and 68 Bq/kg dm. It should be noted that in all cases the bioaccumulation factors of radiocesium in the leaves of *T. cordata* were <1 (from the minimum values of 0.02 in Verhniy Val and to 0.81 in Naberezhno-Khreshchatyts'ka Str.) The BAF of K-40 in leaf samples was in the range from 0.36 (Magnitogors'ka Str.) to 8.6 (Mariinskyi Park). Thus, the obtained data indicate an insignificant contamination of the leaves of the bioindicator species and the moderate contamination of the soils of the city of Kyiv with radiocesium.

During bioindicative investigations the presence of working honey bees was recorded o n flowering trees of *T.cordata* during pollen collection and nectar feeding only in three localitions: Park Feofaniya, Harkivs'ke Ave, 180/21, and Holosiivs'ky Ave. In general, the presence of honey bee in a particular place depends on the location of specialized apiaries, which are quite few in Kyiv. The radius of the flight activity of working bee is 2-3 km, and the area of the working area is 10-12 km^2 [37]. The presence of honey bees in an urbanized environment in immediate proximity to highways threatens the health of a particular bee family, which includes bee-forage, as numerous pollutants from traffic emissions as well as other non-identified contaminants enter the trophic chain. In general, the bee's body is capable of significant accumulation of toxicants, the effect of which on the functioning and performance of the bee is not fully understood. It is clear that an increase in the content of some toxicants negatively affects on the homeostasis of bees. The set of many parameters simulates the toxicity of specific elements. It is believed that Cd can block Ca^{2+} ions and negatively affect the functioning of muscles [38]. Arsenic affects cellular metabolism and can cause oxidative stress, and so on. At the same time, the toxic effects caused by certain pollutants depend on the age of the bee and the season [39, 40, 41].

Most monitoring studies traditionally determine the content of pollutants in bee products (honey, pollen, etc.) and, to a lesser extent, in the body of bees. Therefore, the information about the content of metals in the body of bees is quite limited. The generalization of literary and own data on the content of 23 elements (heavy metals and toxic elements) in bees' bodies is given in Table It should be noted that the presence of some elements (Be, Mg, Ti, V, Ge, Sr, Zr, Mo, Ag, Bi) in the organism *A. mellifera* in the conditions of the urbanized environment was established for the first time (Table 8). Iin some studies mercury in samples was not found that the authors explained by the lack of sources of pollution [42]. At the same time, Sadeghi *et al*.[43]. reports the maximum values of this toxicant and the source of mercury entering the bee's bodies is nectar and pollen of plants, which, in turn, are capable of its accumulation. Generally, in the bees, Mg, Ba, Ag were represented by significant quantity, the average levels were observed for Be, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Se, Zr, Cd (the exception are data of Matin *et al*.[42] for industrial zone), Pb and Hg. The lowest levels are recorded for Li, Bi and Ge. Compare with the data of other authors, in our study, bee's bodies contained the lower values of Cr, Fe, Mn, and Cd. Content of Hg, Pb, Ni, As, and Cu was elevated.

At present, studies of the impact of various concentrations of heavy metals on the bee population are relevant given a widespread and threatening phenomenon such as the Colony Collapse Disorder [44] observed in Europe and America [45], and, recently, in Ukraine (private messages) Since there is currently no clear explanation for this phenomenon, researchers are trying to take into account all possible causes, among which polluting the environment is one of the first places of pollutants.

In Kyiv the plantations of *Tilia spp.* are quite common. The chemical analysis of pollen and nectar of *T. cordata* showed that the quality and quantity of proteins and sugars are not the best nutritional resource for bees, but due to the mass of flowering, especially in urban environments where the vegetation is structurally simplified, nectar and linden pollen are a significant addition to the diet of these insects [46]. Also interesting is the fact that nectar of linden can cause paralysis of honey bees and bumblebees; because it contains mannose, for metabolism of it in an organism of bees has not sufficient enzyme phosphomannosis isomerase [47]. During two years of research, we have not seen dead workers of A. mellifera in close proximity to flowering trees, but we fixed the phenomenon of mass death of bumblebees, which was observed during active flowering *T. cordata* on the left bank of the city. A similar phenomenon was previously recorded in Poland [47]. When designing the planting of the city it should be taken into account that nectar and pollen producing flower of trees are an important chain in the feeding of many organisms and bees in particular, and therefore it is rational to use different types of tree plants that can provide as much as possible a variety of quantitative and qualitative food resources.

The obtained data testify that honey bees are informative indicators of a wide spectrum of toxicants. Data on the presence/absence of *A. mellifera* individuals in localities, the content of their pollutants should be taken into account for the environmental assessment of the environment. However, since sampling was difficult (related to the location and position of the apiaries), and the presence in the ecotops was only partial, in our opinion, A. mellifera should be used as an additional bioindicator, in combination with others, for evaluation the contamination of urban ecosystems.

Activity of radiocaesium in samples of *Apis mellifera* from Park Feofaniya, Harkivs'ke Ave and Holosiivs'ky was below the detection limit (BDL), which completely coincides with values of radionuclide activity in *T. cordata* leaves and directly in the soils from these locations. The activity of ^{40}K was in the range of 80 to 146 Bq / kg dm. Thus, in this chain of test objects, honey bees, as consumers of a believed contaminated feed, have shown qualitatively their indicative properties.

One way or another, for a more complete understanding of the degree of negative impact of technogenic pollution on biota objects, assessment of the consequences of various types of man-made and anthropogenic influences, estimation of "health" of the environment it is possible to recommend the use of a complex of bioindicative species with the use a set of methodological approaches.

Table 1: Sampling sites in the city of Kyiv (2014 and 2015)

Number of location on the map	Ecotope*	Location	Coordinates, altitude, m
		Parks	
1	X11	Park Feofaniya	50°20'24.0"N
			30°29'13.4"E
			153
2	X11	Park Dubky	50°29'12.4"N
			30°25'34.0"E
			170
3	X23	Pushkin Park	50°27'19.3"N
			30°27'16.8"E
			173
4	X23	Mariins'kyi Park	50°26'50.5"N
			30°32'22.8"E
			199
5	X23	Park Nyvky	50°27'34.1"N
			30°24'46.4"E
			181
		Areas adjacent to residential buildings, distance from the road ≤ 20m	
6	J4.6	Kharkivs'ke Ave	50°24'35.9"N
			30°40'06.7"E
			102
7	J4.6	Golosiivs'kyi Ave	50°23'30.9"N
			30°30'14.0"E
			151
8	J4.6	Mytropolyta A.Sheptyts'kogo Str.	50°27'11.9"N
			30°35'47.9"E
			100

		Along the roads with middle traffic	
9	J4.2	Metrologichna Str.	50°21'08.6"N
			30°28'34.1"E
			190
10	J4.2	Verbyts'kogo Str.	50°24'44.8"N
			30°39'02.5"E
			101
11	J4.2	Magnitogors’ka Str.	50°27'15.2"N
			30°38'25.6"E
			104
12	J4.2	Verhniy Val Str.	50°27'47.5"N
			30°30'30.4"E
			117
13	J4.2	Dragomanova Str.	50°24'33.4"N
			30°38'20.5"E
			106
		Along the highways with intensive traffic	
14	J4.2	Peremogy Ave	50°26'51.5"N
			30°29'20.7"E
			129
15	J4.2	Druzhby Narodiv Blvd	50°24'47.0"N
			30°31'56.5"E
			143
16	J4.2	Nauky Ave	50°23'45.2"N
			30°31'54.3"E
			149
17	J4.2	Harkivs'ke Ave	50°24'44.6"N
			30°39'58.8"E
			102
18	J4.2	Grushevs'kogo Str.	50°26'58.8"N
			30°31'49.6"E
			175
19	J4.2	Hreschatyk/Prorizna Str.	50°26'52.1"N
			30°31'18.8"E
			158
20	J4.2	Naberezhno-Hreschatyts'ka Str.	50°28'13.1"N
			30°31'18.4"E
			102
		Industrial location	
21	J6.52	Chervonotkats’ka Str., Factory “Radical”	50°27'33.7"N
			30°38'49.9"E
			105

*Classification of ecotops adopted according to EUNIS[17]: X11 – Large parks, X23 – Large non-domestic gardens, J4.6 – Pavements and recreation areas, J4.2 - Road networks, J6.52 – Industrial scrap and detritus heaps

Table 2: Content of heavy metals in *Tilia cordata* leaves and soils, and the index of stress (IS*) from ecotopes of the Kyiv city

Location*	Leaf (l), soil (s)	Ni, mg/kg dm	Cr, mg/kg dm	Cu, mg/kg dm	Pb, mg/kg dm	Cd, mg/kg dm	Hg, mg/kg dm	IS
Park Feofaniya	l	3.0	3.0	36	3.0	0.03	0.03	0.167
	s	32.0	80.0	180	50.0	0.13	0.03	
Park Dubky	l	8.5	5.0	10	3.8	0.08	0.03	0.132
	s	7.14	6.0	49	40.4	0.24	0.03	
A.S. Pushkin Park	l	2.6	30.0	12	3.1	0.03	0.03	0.216
	s	32.0	44.0	54	60.0	0.13	0.04	
Mariins'kyi Park	l	4.4	4.4	48	3.0	0.03	0.03	0.192
	s	34.0	14.0	54	50.0	0.12	0.03	
Park Nyvky	l	6.95	6.0	22	3.0	0.04	0.03	0.203
	s	18.6	8.0	96	30.0	0.16	0.04	
Kharkivs'ke Ave	l	3.8	3.1	41	3.0	0.06	0.06	0.137
	s	32.0	30.0	84	80.0	0.16	0.06	
Golosiivs'kyi Ave	l	3.2	4.1	18	6.0	0.06	0.05	0.239
	s	60.0	52.0	110	55.0	0.15	0.04	
Mytropolyta A.Sheptyts'kogo Str.	l	3.6	3.2	51	2.4	0.08	0.04	0.201
	s	32.0	50.0	78	50.0	0.14	0.06	
Metrologichna Str.	l	4.8	5.1	51	4.1	0.82	0.76	0.215
	s	54.0	60.0	80	80.0	0.16	0.08	
Verbyts'kogo Str.	l	3.6	3.0	22	2.0	0.04	0.04	0.189
	s	40.0	50.0	80	62.0	0.13	0.06	
Dragomanova Str.	l	12.4	4	33	4.9	0.1	0.05	0.233

	s	24.7	50	85	70.6	0.17	0/08	
Magnitogors'ka Str.	l	2.8	3.1	41	5.1	0.08	0.06	0.138
	s	40.0	60.0	70	80.0	0.15	0.08	
Verhniy Val Str.	l	3.2	4.0	60	3.2	0.04	0.08	0.217
	s	22.0	42.0	54	80.0	0.14	0.04	
Peremogy Ave	l	3.4	4.2	50	3.0	0.1	0.08	0.237
	s	54.0	240	110	58.0	0.16	0.08	
Druzhby Narodiv Blvd	l	2.6	4.1	48	3.1	0.04	0.06	0.187
	s	42.0	42.0	80	82.0	0.14	0.04	
Nauki Ave	l	3.8	3.0	12	30.0	0.06	0.04	0.240
	s	51.0	51.0	210	60.0	0.14	0.04	
Harkivs'ke Ave	l	3.4	3.4	32	2.0	0.06	0.04	0.218
	s	41.0	110	80	60.0	0.14	0.07	
Grushevs'kogo Str.	l	2.6	4.2	22	5.0	0.06	0.04	0.23
	s	50.0	32.0	152	100	0.13	0.06	
Hreschatyk/Prorizna Str.	l	5.8	4.1	11	6.2	0.08	0.06	0.192
	s	50.0	51.0	150	410	0.14	0.06	
Naberezhno-Hreschatyts'ka	l	6.6	5.1	22	5.4	0.09	0.06	0.240
	s	40.0	50.0	112	100	0.16	0.06	
Factory Radical	s	64.0	110	240	110	0.24	1.1	

Table 3: Hazard ratios (HR) of heavy metals in *Tilia cordata* leaves and soils in the city of Kyiv locations

		Leaves							Soil						
		Ni, HR	Cr, HR	Cu, HR	Pb, HR	Cd, HR	Hg, HR	Σ HR	Ni, HR	Cr, HR	Cu,HR	Pb,HR	Cd, HR	Hg, HR	Σ Hr
Parks	Park Feofaniya	0.75	0.5	12	0.15	0.02	0.014	13.43	8	13.33	60	2.5	0.07	0.014	83.91
	Pushkin Park	0.65	5	4	0.155	0.02	0.014	9.84	8	7.33	18	3	0.07	0.018	36.42
	Mariins'kyi Park	1.1	0.73	16	0.15	0.02	0.014	18.01	8.5	2.33	18	2.5	0.06	0.014	31.4
	Park Nyvky	1.74	1	7.33	0.15	0.02	0.014	10.25	4.65	1.33	32	1.5	0.08	0.018	39.58
	Park Dubky	2.13	0.83	3.33	0.19	0.04	0.014	6.53	1.79	1	16.3	2.02	0.12	0.014	21.24
Areas adjacent to residental building	Kharkivs'ke Ave	0.26	0.52	13.67	0.15	0.03	0.03	14.66	8	5	28	4	0.08	0.03	45.11
	Golosiivs'kyi Ave	0.8	0.68	6	0.3	0.03	0.02	7.83	15	8.67	36.7	2.75	0.08	0.02	63.22
	Mytropolyta A.Sheptyts'kogo Str.	0.9	0.53	17	0.12	0.04	0.02	18.61	8	8.33	26	2.5	0.04	0.03	44.9
Along the highways with middle traffic	Metrologichna Str.	1.2	0.14	17	0.21	0.41	0.35	19.31	13.5	10	26.7	4	0.08	0.04	54.32
	Verbyts'kogo Str.	0.9	0.5	7.33	0.1	0.02	0.02	8.87	10	8.33	26.7	3.1	0.07	0.03	48.23
	Magnitogors'ka Str.	0.7	0.52	13.67	0.26	0.04	0.03	15.22	10	10	23.3	4	0.08	0.04	47.42
	Verhniy Val Str.	0.8	0.67	20	0.16	0.02	0.04	21.69	5.5	7	18	4	0.07	0.02	34.59
	Dragomanova Str.	3.1	0.67	11.0	0.25	0.05	0.023	15.09	6.18	8/33	28.33	3.53	0.09	0.036	46.49
Along the highways with intensive traffic	Peremogy Ave	0.85	0.7	16.67	0.15	0.05	0.036	18.46	13.5	40	36.7	2.9	0.08	0.036	93.22
	Druzhby Narodiv Blvde	0.65	0.68	16	0.16	0.02	0.027	17.54	10.5	7	26.7	4.1	0.07	0.018	48.39
	Nauky Ave	0.95	0.5	4	1.5	0.03	0.018	7.0	12.75	8.5	70	3	0.07	0.018	94.34
	Harkivs'ke Ave	0.85	0.57	10.67	0.1	0.03	0.018	12.24	10.25	18.33	26.7	3	0.07	0.032	58.38
	Grushevs'kogo Str.	0.65	0.7	7.33	0.25	0.03	0.018	8.98	12.5	5.33	50.7	5	0.07	0.027	73.63
	Hreschatyk/Prorizna Str.	1.45	0.68	3.67	0.31	0.04	0.027	6.18	12.5	8.5	50	20.5	0.07	0.027	91.6
	Naberezhno-Hreschatyts'ka Str.	1.65	0.85	7.33	0.27	0.05	0.027	10,18	10	8.33	37.3	5	0.08	0.027	60.74
Industrial habitat	Factory Radical								16	18	80	5.5	0.12	0.5	120.12

Table 4: Bio-accumulation factors (BAFs) for heavy metals in *Tilia cordata* leaves from locations in the city of Kyiv

Location	Ni,BAF	Cr,BAF	Cu,BAF	Pb,BAF	Cd,BAF	Hg,BAF
Park Feofaniya	0.09	0.04	0.20	0.06	0.23	1.0
Pushkin Park	0.08	0.68	0.22	0.05	0.23	0.75
Mariins'kyi Park	0.13	0.31	0.89	0.06	0.25	1.0
Park Nyvky	0.37	0.75	0.23	0.10	0.25	0.75
Park Dubky	1.19	0.83	0.20	0.09	0.33	1.0
Kharkivs'ke Ave	0.12	0.10	0.49	0.04	0.38	1.0
Golosiivs'kyi Ave	0.05	0.08	0.16	0.11	0.40	1.25
Mytropolyta A.Sheptyts'kogo Str.	0.11	0.06	0.65	0.05	0.57	0.67
Metrologichna Str.	0.09	0.09	0.64	0.05	5.30	9.5
Verbyts'kogo Str.	0.09	0.06	0.28	0.03	0.31	0.57
Magnitogors'ka Str.	0.07	0.05	0.59	0.06	0.53	0.75
Verhniy Val Str.	0.15	0.10	1.11	0.04	0.29	2.0
Dragomanova Str.	0/5	0.08	0.39	0.07	0.59	0.63
Peremogy Ave	0.06	0.02	0.45	0.05	0.63	1.0
Druzhby Narodiv Blvd	0.06	0.10	0.60	0.04	0.29	1..5
Nauky Ave	0.07	0.06	0.06	0.50	0.43	1.0
Harkivs'ke Ave	0.08	0.03	0.40	0.03	0.43	0.57
Grushevs'kogo Str.	0.05	0.13	0.14	0.05	0.46	0.67
Hreschatyk/Prorizna Str.	0.12	0.08	0.07	0.02	0.57	1.0
Naberezhno-Hreschatyts'ka Str.	0.17	0.10	0.20	0.05	0.56	1.0

Table 5: A range of data on hazard ratios (HR) in soils (s) and *Tilia cordata* leaves (l) from different ecotops in the city of Kyiv

		HRs for Ni	HRs for Cr	HRs for Cu	HRs for Pb	HRs for Cd	HRs for Hg	Σ HRs
Parks	l	0.65-2.13	0.5 - 5.0	3.33 - 16.0	0.15 - 0.19	0.02 - 0.04	0.014	6.53 - 18.01
	s	1.79 - 8.5	1 - 13.33	16.3 - 60	1.5 - 3.0	0.06 - 0.12	0.014 - 0.018	31.4 - 83.91
Areas adjacent to residential buildings, distance from the road ≤ 20m	l	0.26 - 0.9	0.52 -0.68	6.0 - 17.0	0.12 - 0.3	0.03 - 0.04	0.02 - 0.03	7.83 - 18.61
	s	8.0 - 15.0	5.0 - 8.67	26.0 - 36.7	2.5 - 4.0	0.07 - 0.08	0.02 - 0.03	45.11 - 63.22
Along the roads with middle traffic	l	0.7 - 3.1	0.14 - 0.67	7.33 - 20.0	0.1 - 0.25	0.02 -0.41	0.02 - 0.04	8.87 - 21.69
	s	5.5 - 13.5	7.0 - 10.0	18.0 -28.33	3.1 - 4.0	0.07 -0.09	0.03 - 0.04	34.59 - 54.32
Along the highways with intensive traffic	l	0.65 -1/65	0.5 - 0.85	3.67 -16.67	0.1 - 1.5	0.02 - 0.05	0.018 - 0.036	6.18 - 18.46
	s	10.0 -13.5	5.33 -40.0	26.7 -70.0	2.9 - 20.5	0.07 -0.08	0.018 - 0.036	48.39 - 94.34
Industrial habitat	s	16,0	18.0	80	5.5	0.12	0.5	120.12

Table 6: Activity of ^{137}Cs and ^{40}K (Bq/kg dry mass) in leaves (l) and soils (s) from locations of Kyiv in 2015

Location	^{137}Cs	BAF*	^{40}K	BAF
Parks				
Park Feofaniya, leaves	BDL**		84±18	1,38
soil	17±5		61±5	
Mariins'kyi Park, leaves	BDL		104±25	8,6
soil	54±13		12±5	
Pushkin Park, leaves	BDL		104±25	1.96
soil	87±6		53±4	
Park Nyvky, leaves	BDL		51±10	0.83
soil	67±12		61±8	
Park Dubky, leaves	12±5	0.14	49±5	0.92
soil	87±17		53±3	
Areas adjacent to residential buildings, distance from the road ≤ 20m				
Kharkivs'ke Ave, leaves	BDL		73±13	4.05
soil	11±2		18.6	
Golosiivs'kyi Ave, leaves	BDL		31±12	0.62
soil	76±9		65±5	
Mytropolyta A.Sheptyts'kogo Str. , leaves	9±2	0.11	55±6	1.41
soil	81±5		39±3	
Along the roads with middle traffic				
Metrologichna Str., leaves	BDL		61±5	1.22
soil	15±2		50±3	
Verbyts'kogo Str., leaves	BDL		34±8	0.69
soil	56±5		49±5	
Magnitogors'ka Str., leaves	20±6	0.06	17±3	0.36
soil	300±56		46±5	
Verhniy Val Str., leaves	15±2	0.02	70±4	1.34
soil	238±45		52±14	
Dragomanova Str.	5±1	0.45	39±7	0.47
soil	11±5		82±15	
Along the highways with intensive traffic				
Peremogy Ave, leaves	10±4	0.62	137±32	2.44
soil	16±5		56±9	
Druzhby Narodiv Blvd, leaves	BDL		82±16	1.74
soil	17±2		47±3	
Nauky Ave, leaves	10±3	0.12	73±12	1.37
soil	81±5		53±3	
Harkivs'ke Ave, leaves	BDL		68±15	1.28
soil	97±5		53±3	
Grushevs'kogo Str., leaves	BDL		104±21	
soil	157±39		39±8	
Hreschatyk/Prorizna Str., leaves	BDL		122±30	2.59
soil	31±4		47±5	
Naberezhno-Hreschatyts'ka Str., leaves	18±5	0.81	148±21	2.17
soil	22±4		68±4	
Industrial zone				
Factory Radical, soil	14±2		75±4	

*BAF – Bio-accumulation factor, **BDL – below detection limit

Table 7: Mineral content of *Apis mellifera* bodies

Element	Content, mg/kg dm												Reference
	trace	>0,005 - 0,01	>0,01-0,10	>0,1-1	>1-10	>10-20	>20-50	>50-70	>70-100	>100-300	>300-500	>500	
Li		■											Original data (OD)
			■										[43]
Be			■	■									OD
Mg												■	OD
Ti					■								OD
V				■									OD
Cr				■									[48]
					■								[49, 50], OD
Mn											■		OD
							■						[48]
				■									[43]
Fe					■								[43]
							■						[50]
											■		[48]; OD
Ni					■								[48]
Cu					■								[50]
						■							[48]
							■						[49]; OD
Zn						■							[50]
							■						[48]; OD
Ge		■											OD
As			■										[43]; OD
				■									[42]
Se				■									OD
					■								[49]
Sr					■								OD
Zr				■									OD
Mo			■										OD
Ag								■					OD
Cd	■												[50]
		■											OD
				■									[48, 49]
												■	[42]
Ba										■			OD
					■								[43]
Hg			■										OD
					■								[43]
Pb					■								[42, 48, 49]
				■									[50]
		■											OD
Bi		■											OD

OD* - original data

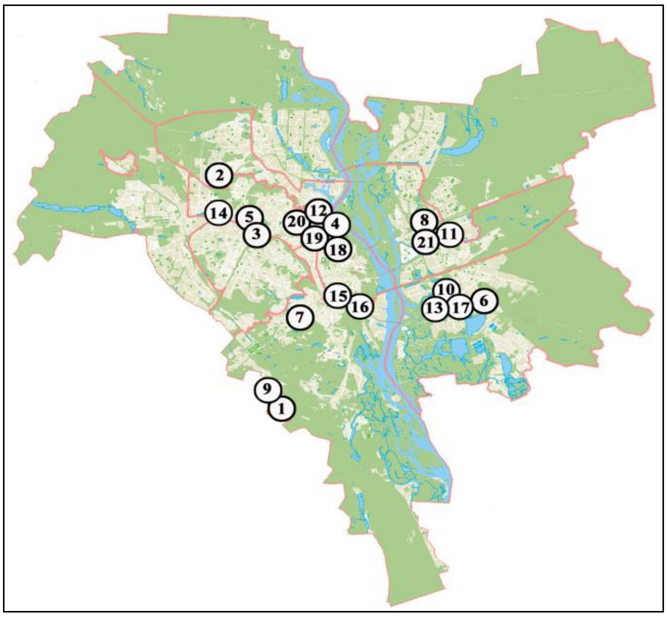

Fig 1: Sampling sites in Kyiv

Conclusions

The analysis of the data obtained shows the complex nature of the pollution of the soils of Kyiv with a complex of heavy metals and radionuclides, and the contamination of nickel, copper and chromium, apparently, is one of its determining factors.

Even only for six studied heavy metals in the soils of Kyiv (Ni, Cr, Cu, Pb, Cd, and Hg) the total excess of permissible levels (hazard ratios) were in the range of 21.24 to 120, 12 in soils, and in *T. cordata* leaves - of 6.53 to 21.69.

A promising approach for background monitoring and assessment of the consequences of various types of man-made and anthropogenic influences is the assessment of "health" of the environment with the use of a complex of bioindicative species.

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