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OCCURRENCE, AND SOURCES OF PERSISTENT ORGANIC POLLUTANTS IN UPPER URBAN SOIL OF CLUJ-NAPOCA, ROMANIA

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ABSTRACT. Most persistent organic pollutants (POPs) were made for specific purposes due to certain characteristic and properties. They can cause various diseases and are problematic for the environment due to their high persistence and toxicity. This study attests the presence of three classes of POPs namely polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in the upper urban soils of Cluj-Napoca, Romania. Soil samples were collected from 10 sampling points areas with heavy traffic. For determination of the compounds, gas chromatography coupled with mass spectrometry and with electron capture detector was used. The obtained results indicate a low level of pollution, the concentrations ranging between 8.83–184.92 ng/g for PAHs, 5.36–112.35 ng/g for PCBs, and 25.96–334.83 ng/g for OCPs. To identify the pollution emission sources, different PAHs and OCPs diagnostic ratios have been applied.

Key words: *persistent organic pollutants, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, organochlorine pesticides, upper urban soil*

INTRODUCTION

Around half of the world's population lives in urban areas, and by 2050, an increase to 68.7% is expected (Luo et al., 2012). Anthropogenic pollution has been created by human society due to industrialization, urbanization and transportation (Orazi et al., 2020).

Persistent Organic Pollutants (POPs) are ubiquitous compounds that have caused concern worldwide, and for almost one hundred years, they have been produced and used for various industries and agriculture. They represent a serious negative impact in a series of adverse effects on both human and environmental health (Barakat et al., 2013).

An important factor for both humans and environment is the soil, having many functions: bio-chemical transformations, the cycle of elements, water filtration, support for plants, infrastructure and for recreational activities (Metfaul et al., 2020). In this regard, in the global cycle of persistent organic pollutants (storage, redistribution, transfer), soil has a significant role, the organic matter being the "sink" of POPs in the soil matrix and in the same time it is the secondary source of POPs too, due to natural phenomena, being carried by the winds, reaching very large distances from their initial area (Ma et al., 2011).

Among the classes of persistent organic pollutants, the most commonly found are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs). They are most often of anthropogenic nature, and their toxicity is attested by their inability to biodegrade, semi-volatile nature and by the fact that they are carried over very long distances, they can bioaccumulate and biomagnify in adipose tissues (Pokhrel et al., 2018).

PCBs, considered "legacy POPs" are a group of 209 compounds, each having between 1 and 10 chlorine atoms grafted onto the structure, called congeners, and depending on the position and number of chlorine atoms they can present different toxicity and physico-chemical properties. They are considered human carcinogens, endocrine disruptors, and neurotoxins and can negatively affect human and ecosystems health (Wang et al., 2017; Jafarabadi et al., 2019; Bartlett et al., 2019). PCB congeners: PCB-77, -81, 105, -114, -118, -123, -126, -156, -157, -167, -169 and -189 presents a level of toxicity comparable to that of dioxins (Saija et al., 2016).

Organochlorine pesticides are also a part of the persistent organic pollutant category. Some OCPs compounds have been included in the “dirty dozen” list of the Stockholm Convention from 2001. The representatives have decided to take all measures necesary to reduce, to eliminate, and to stop the production of aldrin, chlordane (CHL), dieldrin, endrin, heptachlor, dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB), mirex and toxaphene. Hexachlorocyclohexane (HCH) was also added later, along with the isomers α-HCH, β-HCH, γ-HCH (Saija et al., 2016; Bandow et al., 2020). OCPs have been used in industry, agriculture and pest control (Joseph et al., 2020; Yu et al., 2020; Neves et al., 2018). Following continuous exposure to OCPs, endocrine, reproductive and nervous system dysfunctions were observed (Joseph et al., 2020;).

PAHs form a group of ubiquitous and persistent toxic organic pollutants with mutagenic and carcinogenic potential, consisting of two or more condensed benzene nucleus with various structures (Wang et al., 2020; Orazi et al., 2020; Neroda et al., 2020). They can be divided into two categories: PAHs with low molecular mass (LMW) containing between 2 and 4 aromatic rings, which are volatile, and those with high molecular mass (HMW) having between 4-6 aromatic rings, being generally found in solid form (Orazi et al., 2020). The most well known are: 2 rings: Naphthalene (Nap), 3 rings: Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fle), Anthracene (An) and Phenanthrene (Ph), 4 rings: Fluoranthene (Flu), Pyrene (Pyr), benz [a]anthracene (BaA), and Chrysene (Chr), 5 rings: Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), and Dibenz[a,h]anthracene (DahA), 6 rings: Benzo[ghi]perylene (BghiP) and Indeno[1,2,3-cd]pyrene (Ind) (Neroda et al., 2020).

PAHs can result from anthropogenic activities (burning of gasoline, coal, wood and waste, use of oils) and natural activities (forest fires, volcanic eruptions, oil spills, the activity of microorganisms) (Wang et al., 2020). The majority of PAHs are of pyrogenic origin, formed following the thermal decomposition and recombination of organic molecules (pyrolysis and pyrosynthesis), and petrogenic origin formed during the oil maturation process, at low temperatures (Neroda et al., 2020).

Over time, countless studies have been developed on the soils of rural or industrial areas (Croes et al. 2012; Pozo et al. 2012; Wong et al.2009). The tendency was to analyze areas that already had a history of using specific pesticides, or industrial areas whose processes lead to the production of residues with a high content of PCBs. This is how the need to analyze urban soils appeared, to be able to get an idea about the areas where there is no intensive agriculture and no industry at a high level (Pokhrel et al., 2018; Yu et al., 2020).

However, regarding the evaluation of urban soil pollution in Romania, few studies have been done (Covaci et al., 2001; Preda et al., 2011; Tarcau et al., 2013; Ivanescu, 2015). Therefore, this study aims to evaluate the prevalence of persistent organic pollutants (PAH, PCB, POC) in the upper soil within the area of Cluj-Napoca, as well as to identify the sources of POPs pollution in urban environment.

MATERIALS AND METHODS

Chemicals and reagents

In this study, standard mixtures of different types of POPs have been used for qualitative and quantitative analysis. EPA CLP Organochlorine Pesticide Mix (2000 µg/mL in hexane:toluene (1:1 *v/v*)) containing 20 compounds: Tecnazene, α-HCH, Hexachlorobenzene, γ-HCH, Quintozene, Heptachlor, Aldrin, Heptachlor exo-epoxide, Heptachlor endo-epoxide, Trans-Chlordane, 2,4′-DDE, α-Endosulfan, Cis-Chlordane, Dieldrin, 4,4′-DDE, 2,4′-DDD, Endrin, β-Endosulfan, 2,4′-DDT, 4,4′-DDT was provided by Supelco (Merck Romania SRL, Bucharest, Romania). A mix of 12 PCB congeners (10 µg/mL, in heptane): PCB-18, -28, -31, -52, -44, -101, -114, -149, -153, -138, -180, -194 was obtained from Supelco (Merck Romania SRL, Bucharest, Romania). CRM EPA Method 8310 PAH Mixture (500 µg/mL, in acetonitrile:toluene mixture (92:8 *v/v*)), containing a number of 16 compounds such as: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphtene (Ace), Fluorene (Fle), Phenanthrene (Phe), Anthracene (An), Fluoranthene (Flu), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (BaP), Dibenz[a,h]anthracene (DahA), Benzo[g,h,i]perylene (BghiP), and Indeno[1,2,3-cd]pyrene (Ind) was purchased from Restek (Restek Corporation, Bellefonte, United States). Silica, alumina, granular anhydrous sodium sulphate (Merck, Germany), copper of 99.5% purity (Sigma-Aldrich, Merck, Germany) were used. The reagents used in the analysis were acetone, acetonitrile, dichloromethane, and hexane, acquired from Merck (Germany).

Sample collection

The city of Cluj-Napoca is located in the central area of Transylvania, in the basin of Someșul Mic, in northwestern Romania. At the beginning of March 2020, 10 soil samples were collected from the upper soil layer (0-20 cm). To minimize sampling errors, each sample was a mix of 5 other smaller samples from an area of 1x1 m^2. A metal scoop was used for collection, and soil samples were stored in clean zip-lock plastic bags, transported to the laboratory and stored at 4°C until extraction. The location of each sample and each point it was collected from and geographical coordinates is shown in table 1.

Table 1. *Location of sampling points*

Sample Code	Sample Descriptor	GIS Coordinates
S1	Fany bus station	46°47’06.5”N; 23°34’55.2”E
S2	Bio-Nano-Science Institute	46°47’47.1”N; 23°36’15.8”E
S3	Iulius Mall park	46°46’22.7”N; 23°37’33.0”E
S4	Expo Transilvania park	46°46’53.2”N; 23°37’58.5”E
S5	Botanical Garden Alexandru Borza	46°45’45.3”N; 23°35’19.5”E
S6	Faculty of Environmental Science and Engineering	46°46’04.7”N; 23°32’59.5”E
S7	Str. Calea Florești	46°45’25.3”N; 23°32’36.4”E
S8	Unirii Square	46°46’11.0”N; 23°35’22.4”E
S9	Str. Observator	46°45’21.8”N; 23°35’46.2”E
S10	Mărăști square	46°46’42.9”N; 23°36’51.4”E

Sample preparation

The collected soil samples were left at room temperature for 24h to dry, the plant remains were removed and then they were grated. For the extraction of target compounds, 8 g of soil sample were spiked with 100 ng mixture 1 (Naphthalene-d8, Anthracene-d10, Fluoranthene-d10 and Perylene-d12) and 20 ng PCB-30 followed by the addition of 30 mL mixture of acetone:*n*-hexane (1:1, *v/v*), and ultrasonicated for 20 minutes. The sample was subjected to centrifugation for 5 minutes (3000 rpm) and the supernatant was collected. The extraction procedure was repeated 2 more times with fresh solvent mixture. The three extracts collected were combined and left overnight with 1 g of copper for desulphurization. The following day, 10 mL of *n*-hexane was added, the copper was removed by decantation and the resulting extract was concentrated to approximately 2 mL via rotary evaporation, and subjected to the purification procedure, (Barhoumi et al., 2019).

A purification column (from top to bottom) consisting of 1 g anhydrous sodium sulfate, 4 g of activated alumina, and 4 g silica gel was used. The column was conditioned with 20 mL of hexane, after which the sample is loaded into the column. The compounds (PAHs, PCBs, OCPs) are eluted from the column with 20 mL of hexane and 40 mL of a mixture of *n*-hexane:dichloromethane (80:20, *v/v*). The obtained fraction is concentrated on a rotary evaporator to 1-2 mL, then spiked with 100 ng of PAHs multistandard mixture (IS2) (Acenaphtene-d10, Phenanthrene-d10 and Chrysene-d12) and 20 ng of PCB-155 and evaporated to dryness under a stream of nitrogen. The residue is redissolved with 300 μL of *n*-hexane:dichloromethane (80:20, *v/v*), and the resulting sample is analyzed by GC-MS, respectively GC-ECD.

For the quantification of OCPs and PCBs, PCB-30 and PCB-155 were used as internal standards. As for PAHs, a deuterated standard (IS1) to assess the extraction recovery and another one (IS2) containing 3 deuterated compounds for quantitative analysis of PAHs respectively.

Instrumentation

For the determination of polycyclic aromatic hydrocarbons, the obtained extracts were analyzed by gas chromatography coupled with mass spectrometry using a GC-MS with an autosampler (Thermo Eletron Corporation DSQII; Focus GC; TriPlus Autosampler). X-Calibur software was used for the acquisition of data. The separation was performed on a TR-5 MS column (30 m x 0.25 mm x 0.25 µm i.d.) starting from initial temperature of 60°C with a temperature gradient of 10°C/min up to 130°C and 3°C/min up to 300°C. The temperature of the ionization source was 200°C, the transfer line 300°C, and the injector temperature 310°C, the ionization current was 70 eV. Selected ion monitoring (SIM) mode was used for data acquisition. The injection volume was 1 µL, splitless, with helium as carrier gas at a constant flow of 1.2 mL/min.

For OCPs and PCBs, the analysis was performed by GC-ECD, using a gas chromatograph model Trace GC equipped with a ^{63}Ni electron capture detector, and a TriPlus Autosampler (Thermo Electron Corporation). Acquisition of data was performed using Chrom-Card software. The separation was carried out on a capillary column model HP-5MS (30 m x 0.25 mm i.d., 1.0 µm film thickness, Agilent). The gradient temperature program was 70°C to 180°C at a rate of 25°C/min, from 180 to 200°C at 1°C/min, from 200 to 260°C at a rate of 2°C/min, and from 260 to 300°C at 5°C/min with a holding time of 5 min at 300°C. The carrier gas was nitrogen with a constant flow rate of 2 mL/min. The temperatures of the injector and detector were set at 270°C and 300°C. Identification of OCPs and PCBs compounds was made on the retention time of the standard mixtures.

RESULTS AND DISCUSSIONS

PAH concentrations in soil samples

Throughout the 10 analyzed samples, we detected all the compounds. The richest sample in PAHs is S10, where we had a total PAHs concentration of 126.53 ng/g, being the only sample out of the 10, in which we found all the compounds from the standard list. There were 3 samples that lacked in PAHs diversity, namely S2, S3, S6, which only had 12 out of the 16 standard compounds present.

The sample with the highest concentration was S7 with 184.92 ng/g, while S8 is the second one with 178.71 ng/g. Both of them are situated very close to the most circulated roads from Cluj-Napoca, so that might be the best way to explain these values. The lowest concentration found was in sample S5, with 8.83 ng/g, sample which was taken from the botanical garden. The low value compared to the other samples is obvious, because the botanical garden represents an area with high vegetation, containing plants which are beneficial for the air quality improvement (table 2).

The PAH diagnostic ratios were applied for the identification of their sources. Ratios of ΣLMW/ΣHMW (sum of PAH with LMW and sum of PAH with HMW) were calculated, and it appears that petroleum is the source in all analyzed samples (figure 1). If the ΣLMW/ΣHMW ratio is greater than 1 the source is petrogenic (fossil fuels, oil and coal), and if the ratio is less than 1, the source is pyrogenic (combustion processes and volcanoes) (Zhang et al., 2008).

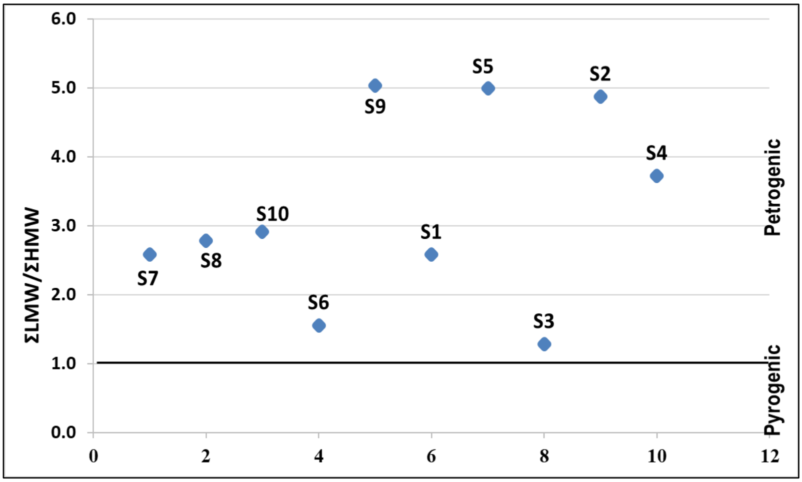

Fig. 1. *Isomeric ratios of ΣLMW/ΣHMW*

Secondly, the results from the An/(An+Ph) ratio had a value under 0.1 which usually indicates a petrogenic source, and greater than 0.1, a pyrogenic nature. A ratio of Flu/(Flu+Pyr) below 0.4 indicates a petrogenic source, ratios between 0.4 and 0.5 are more characteristic to fossil fuels combustion and greater than 0.5 indicates grass/wood/coal combustion (Orazi et al., 2020). These values can be explained by the fact that BbF and Ind are markers for diesel engines, and for gasoline engines, Ind, Ph, Flu, Pyr and An are specific markers of coal and biomass combustion, and Nap results mainly from incomplete combustion (Zhang et al., 2008; Orazi et al., 2020).

From the ratios of An/(An+Ph) and Flu/(Flu+Pyr) the results suggest that the PAHs present at samples S8 and S2 are of pyrogenic nature, S10, S3, and S6 are from combustion of fossil fuels, S1, S7, S5, and S4 are from combustion of petroleum, coal, biomass, and the sample S9 is of petrogenic source (figure 2).

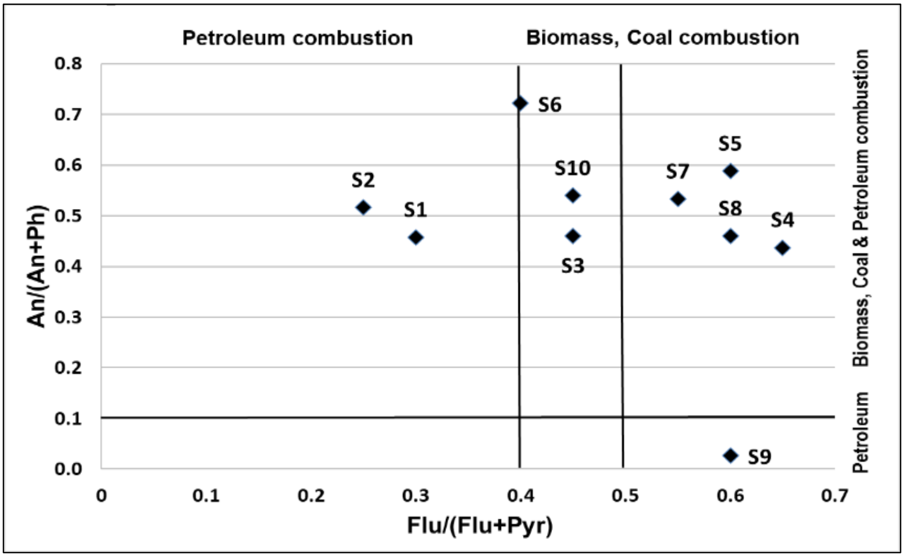

Fig. 2. *Isomeric ratios of An/(An+Ph) versus Flu/(Flu+Pyr) in soil samples*

Table 2. *Concentrations of polycyclic aromatic hydrocarbons (ng/g soil) in different sampling points*

Compound	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Nap	27.52	20.60	3.23	24.40	0.97	26.13	12.04	13.19	20.30	21.01
Acy	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.24
Ace	0.88	nd	nd	nd	0.10	nd	2.14	2.14	1.19	0.28
Fle	0.31	0.94	0.32	0.31	0.48	0.10	5.25	3.69	1.13	0.89
Ph	25.90	29.33	12.76	5.22	4.00	2.28	51.21	44.96	18.84	39.49
An	11.10	9.78	10.44	9.69	6.00	1.52	62.59	67.44	28.26	32.31
Flu	7.92	1.93	2.32	1.22	1.66	0.10	7.38	15.89	0.06	15.18
Pyr	9.40	1.81	2.72	1.57	0.64	0.07	6.46	18.66	2.22	12.95
Chr+BaA	0.21	0.04	0.28	0.08	0.85	0.19	4.93	8.74	0.07	1.77
BbF + BkF	0.13	0.15	0.38	0.21	0.15	0.04	0.95	1.92	0.42	1.72
BaP	7.74	8.45	15.11	7.29	0.09	6.85	22.81	0.17	10.25	0.25
BghiP	nd	nd	nd	nd	nd	nd	7.50	1.47	0.69	0.10
Ind	0.04	nd	0.05	0.25	0.04	nd	1.39	0.29	0.08	0.02
DahA	0.05	0.07	nd	0.02	0.01	0.01	0.24	0.19	0.07	0.38
Total PAHs	91.18	73.14	47.59	50.28	8.83	43.51	184.92	178.71	83.61	126.53
LMW/HMW	2.58	4.87	1.28	3.72	4.99	1.56	2.58	2.78	5.03	2.91
An/(An+Ph)	0.3	0.25	0.45	0.65	0.6	0.4	0.55	0.6	0.6	0.45
Flu/(Flu+Pyr)	0.46	0.52	0.46	0.44	0.59	0.72	0.53	0.46	0.03	0.54

nd- not detected

PCBs concentrations in soil samples

From all of the analyzed samples, the highest PCBs values were PCB-31 (nd–39.63 ng/g), PCB-44 (nd–27.14), and PCB-52 (nd–47.65). These three were abundant in all samples in comparison to the other PCBs from the standard. PCB-101 and PCB-114 were undetectable in any of the analyzed samples.

There were three samples that had the highest concentrations of PCBs: S4 (112.35 ng/g); S10 (106.48 ng/g); and S3 (79.28 ng/g), all of them being close to one another (distances of hundreds of meters between them). The best explanation for these values could be their positions and that there are industrial emissions from the nearby production of electronic equipment's, since this area is relatively close to the industrial parks like Tetarom 2 and Emerson. Meanwhile, the samples with the lowest concentrations were S7 (5.36 ng/g), S1 (12.31 ng/g), and S2 (31.21 ng/g) (table 3).

Low molecular weight PCBs are used in transformers, capacitors, and lubricants and high molecular weight PCBs are commonly used in paints and plasticizers (Xu et al., 2019). This suggest that the PCBs found in this study are from plastic or paint manufacturing and from electrical capacitors. To understand the extent of PCBs pollution, more information is needed due to the small number of PCBs and samples analyzed, requiring more detailed studies in the future.

Table 3. *The concentrations of polychlorinated biphenyls (ng/g soil) found in different sampling points*

Compound	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
PCB-18	1.22	nd	7.80	22.23	nd	nd	nd	nd	nd	19.29
PCB-31	1.21	11.78	20.20	18.39	12.01	nd	1.29	nd	14.76	39.63
PCB-28	0.87	7.37	5.14	5.90	nd	nd	0.70	10.44	7.40	7.60
PCB-44	1.54	7.59	15.43	4.97	8.84	nd	nd	21.12	21.17	27.14
PCB-52	nd	nd	3.56	47.65	19.10	13.73	0.97	7.44	3.29	8.90
PCB-101	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB-114	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB-149	nd	nd	nd	nd	nd	12.25	0.76	0.42	nd	0.27
PCB-153	5.60	1.58	24.90	10.58	10.52	4.27	0.05	9.72	1.75	2.12
PCB-138+180	1.10	0.91	0.85	0.47	0.43	3.92	0.87	1.68	0.47	0.92
PCB-194	0.77	1.95	1.41	2.17	0.84	3.40	0.73	2.48	0.31	0.60
∑PCBs	12.31	31.21	79.28	112.35	51.74	37.58	5.36	53.29	49.15	106.48

nd- not detected

OCPs concentrations in soil samples

Twenty-one organochlorine pesticides were determined in the analyzed samples with a concentration of total OCPs ranging from 58.24 ng/g soil in sampling point S2 to 334.83 ng/g soil in sampling point S6. The most encountered compounds were 4’4-DDT (nd-88.28 ng/g soil), α-HCH (2.65-47.10 ng/g soil) and Heptachlor-exo-epoxide (1.17-43.34 ng/g soil), with the highest values being found in samples S6 and S4 (table 4). Other compounds with high concentrations were HCB (1.32-54.68 ng/g soil) and Heptachlor (0.69-25.07 ng/g soil), the highest values being found in S10 and S4 for HCB and S4 and S5 for heptachlor. The least encountered compounds were β-endosulfan (9.22 ng/g soil), 2’4-DDE (1.02 ng/g soil), and Heptachlor-endo-epoxide (0.24 ng/g soil), each being found only in one sample, β-endosulfan and Heptachlor-endo-epoxide in S9, and 2’4-DDE in S8. Methoxychlor, 2’4-DDT, and α-Endosulfan were not detected in any of the samples.

For a better estimation of the type of OCPs used, the analyzed compounds were divided as follow: HCH residues (*α*- and *γ*-HCH); DDT residues (2*,*4`-DDT, 4*,*4`-DDT, 2*,*4`-DDD, 4*,*4`-DDD, 2*,*4`-DDE, Methoxychlor); Endosulfan residues (*α*- and *β*-Endosulfan); Chlordane related compounds residues (*cis*-Chlordane *(CC)*, *trans*-Chlordane (TC), Heptachlor and Heptachlor Epoxide) and Cyclodiene pesticides residues (Aldrin, Dieldrin, Endrin).

α-HCH (2.65–47.10 ng/g) was found in all analyzed samples and γ-HCH isomer was only found in two samples (S1 and S6) indicating the use of the HCH technical mixture instead of pure lindane (γ-HCH). HCB (1.32–54.68 ng/g) was also found in all analyzed samples, indicating their use together as technical HCH.

Aldrin was used to control pests, and following the transformation processes it transforms in Dieldrin (Meftaul et al., 2020; Joseph et al., 2020). Concentrations of Aldrin were found in S10 (5.33 ng/g), S8 (6.23 ng/g) and S9 (5.15 ng/g), and Dieldrin in S3 (20.50 ng/g), S6 (84.37 ng/g), S7 (1.00 ng/g) and S8 (6.43 ng/g). Endrin was detected in samples S9 (1.13 ng/g) and S6 (10.43 ng/g), indicating historical pollution.

Due to the very low rate of degradation and persistence of 4,4-DDT, 4,4-DDE and 4,4-DDD which are its metabolites are usually identified together in the analyzed samples. A possible route of exposure is construction materials that contain and gradually release these substances in the environment (Bandow et al., 2020). 4,4-DDT was detected in almost all samples, missing only from sample S2, with values between 0.81–88.28 ng/g soil, while 2,4-DDT was not detected in any of the samples. 2,4-DDD (nd–20.55 ng/g soil) was prevalent, missing only from one sample, namely S6. 4,4-DDD (nd–33.97 ng/g soil) was found only in four samples, S3, S6, S7 and S10. 2,4-DDE could only be found in one sample, S8 with a value of 1.02 ng/g soil.

Four ratios were calculated to identify the sources of OCPs such as: ΣDDTs/ΣHCHs, α-HCH/γ-HCH, (DDE + DDD)/ΣDDTs, and CC/TC (Hitch and Day, 1992; Lee et al., 2001; Jiang et al., 2009; Sultana et al., 2014) (table 5).

The results from the first ratio, ΣDDTs/ΣHCHs, are used to determine which if the important source of OCPs, and mainly to establish the dominance of DDTs or HCHs. A ratio value higher than 1 reflects a long term usage of DDTs, while a value lower than 1 approves the use of HCHs (Barhoumi et al 2019). Values under 1 were found in three out of ten samples, respectively in S2, S8, and S9.

The ratio of α-HCH/γ-HCH can be used as an indicator of the source of HCH but also to determine the history of HCH use. If the result of the α-HCH/γ-HCH ratio is closer to 0, it attests a presence of a higher amount of lindane (γ-HCH) in the sample. Between the values of 1 and 3, it may indicate that the input of HCH was a mixture of technical HCH and lindane. If the value is greater than 4, it means that technical HCH is predominant (Law et al. 2001). In the case of this study, there are only two samples in which we could find γ-HCH, so the value of this ratio could only be established for two samples, S1 (4.32) and S6 (9.27), from both resulting values that attest the use of technical HCH instead of lindane.

(DDE + DDD)/ΣDDTs ratio is mostly used to determine the source of DDTs. If the ratio result is greater than 0.5, then a historical accumulation of DDT is attested, while values lower than 0.5 could suggest recent discharges

(Kassegne et al. 2020). In this study, S2, S5, S7 and S10 confirm the presence of historical DDT sources, with values higher than 0.5, while the other 6 samples prove the presence of recent DDTs.

CC/TC ratio is used to indicate the type of chlordane present in a sample. Values over 1 correspond to technical mixture, meaning that trans-chlordane has a higher presence in samples, while values under 1 attest a higher presence of cis-chlordane (Lee et al. 2001). In our case, all the samples had values higher than 1, which corresponds to technical mixture.

The Romanian environmental law (OM no. 184/1997) provides that acceptable soil concentration of α-HCH must not exceed 100 ng/g, and DDT 250 ng/g, for residential use. In the case of the carried study these values are not exceeded, which makes them appropriate.

Table 4. *The concentrations of organochlorine pesticides (ng/g soil) from different sampling points*

Compound	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Tecnazene	0.68	7.69	13.66	14.76	12.42	8.86	0.48	5.55	4.39	9.90
α-HCH	2.65	28.63	20.51	46.21	35.82	47.10	2.90	31.53	26.43	20.00
HCB	4.62	1.32	34.17	11.85	2.25	4.01	1.89	2.41	19.08	54.68
γ-HCH	0.61	nd	nd	nd	nd	5.08	nd	nd	nd	nd
Quintozene	nd	nd	nd	nd	nd	1.56	0.09	6.14	nd	1.74
Heptachlor	0.69	9.27	8.18	25.07	21.88	7.83	2.22	13.97	20.35	10.56
Aldrin	nd	nd	nd	nd	nd	nd	nd	6.23	5.15	5.33
Heptachlor-exo	28.66	4.65	27.62	62.08	4.55	43.34	4.59	1.17	11.17	4.54
Heptachlor-endo	nd	nd	nd	nd	nd	nd	nd	nd	0.24	nd
Trans-Chlordan	7.17	2.99	8.37	19.35	19.24	nd	0.89	nd	1.25	3.07
α-Endosulfan	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cis-Clordan	8.01	nd	20.10	21.59	19.80	nd	2.26	nd	1.47	4.39
Dieldrin	nd	nd	20.50	nd	nd	84.37	1.00	6.43	nd	nd

Compound	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
Endrin	nd	nd	nd	nd	nd	10.43	nd	nd	1.13	nd
β-endosulfan	nd	nd	nd	nd	nd	nd	nd	nd	9.22	nd
2,4-DDE	nd	nd	nd	nd	nd	nd	nd	1.02	nd	nd
2,4-DDD	8.69	3.68	17.84	17.10	20.55	nd	3.30	3.14	3.89	6.71
4,4-DDD	nd	nd	2.90	nd	nd	33.97	1.14	nd	nd	3.73
2,4-DDT	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
4,4-DDT	23.15	nd	20.19	70.50	60.26	88.28	5.27	0.81	4.81	14.97
Methoxychlor	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
∑OCPs (ng/g)	84.93	58.24	194.04	289.41	196.75	334.83	25.96	78.42	108.45	139.6

nd- not detected

Table 5. *Distribution of organochlorine pesticides in urban soils*

Sample Code	**ΣHCHs (ng/g)**	**ΣDDTs (ng/g)**	**ΣEndosulf (ng/g)**	**ΣChlordane (ng/g)**	**ΣCyclodiene (ng/g)**	**ΣDDTs/ ΣHCHs**	**α-HCH/ γ-HCH**	**(DDE+DDD)/ ΣDDTs**	**CC/TC**
S1	3.26	31.84	nd	15.18	nd	9.76	4.32	0.27	1.12
S2	28.63	3.68	nd	3.00	nd	0.13	nd	1	nd
S3	20.50	40.93	nd	28.47	20.50	2.00	nd	0.51	2.40
S4	46.21	88.5	nd	40.94	nd	1.92	nd	0.2	1.12
S5	35.82	80.81	nd	39.04	nd	2.26	nd	0.25	1.03
S6	52.18	122.25	nd	nd	94.80	2.34	9.27	0.28	nd
S7	2.89	9.66	nd	3.15	1.0	3.34	nd	0.45	2.53
S8	31.53	4.96	nd	nd	12.66	0.16	nd	0.84	nd
S9	26.43	8.62	9.22	2.72	6.28	0.33	nd	0.44	1.17
S10	19.99	25.41	nd	7.46	5.33	1.27	nd	0.41	1.43

nd- not detected

Following the obtained results, we can conclude that in the area of the city of Cluj-Napoca we meet different values of POPs, depending on the area of the sampling and the intensity of anthropic activities (figure 3).

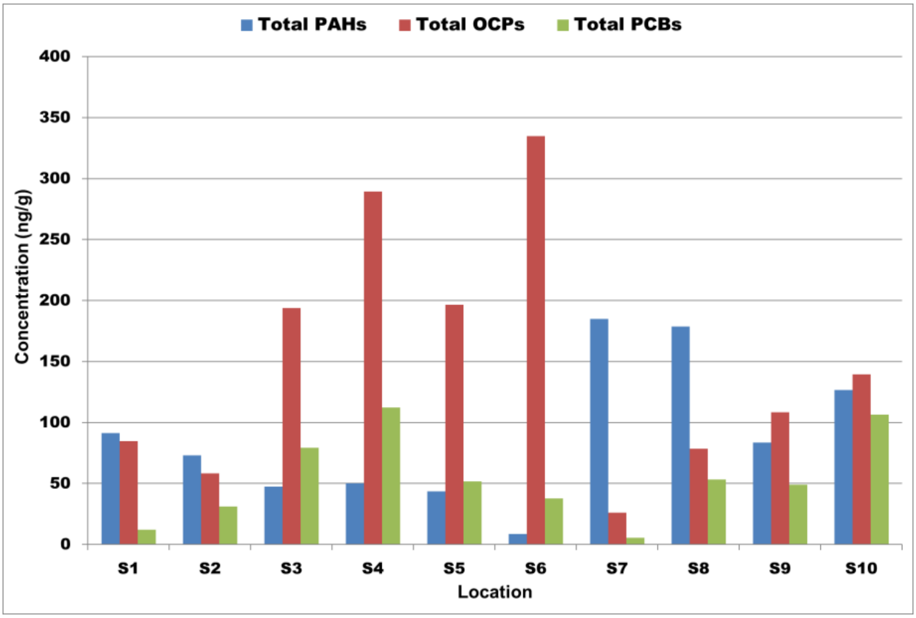

Fig. 3. *The concentration of POPs found in the soil samples*

Other studies performed in Romanian show the presence of POPs in urban soil as follow:

- different regions of Romania, (ΣHCH 28.4±33.7 ng/g; ΣDDT 226.9±157.2 ng/g; ΣPCBs 4.0±2.5 ng/g) (Covaci et al., 2001);
- Bucharest PCBs 0.5–21.3 ng/g, (Preda et al., 2011) and PCBs 1.1–128 ng/g (Ivanescu, 2015);
- eastern Romania, (ΣDDT: 4.4–79 ng/g; ΣHCH 1.1–9.8 ng/g), (Tarcau et al., 2013).

Comparing the results of these studies we can conclude that the concentrations of PCBs found in Cluj-Napoca (PCBs: 5.36–112.35 ng/g) are lower than the ones found in Bucharest by Ivanescu (2015), but higher than the ones found by Preda (2011). For the ΣDDT, the concentrations found in Cluj-Napoca (3.68–122.25 ng/g) are lower than the ones found by Covaci (2011) in urban soils from Romania, but the concentrations of ΣHCH in Cluj-Napoca (2.89–46.21 ng/g) are higher than the ones found by Covaci (2011) and Tarcau (2013).

CONCLUSIONS

In the present study we assessed the widespread distribution of PAHs, PCBs and OCPs, even though they were banned many years ago. The concentration of POPs in the surface soils of Cluj-Napoca according to the class of compounds found are between 8.83 and 184.92 (ng/g) for PAHs, between 5.36 and 112.35 (ng/g) for PCBs, and between 25.96 and 334.83 (ng/g) for OCPs.

The presence of pollutants in the urban environment can be explained by the burning of fossil fuels, atmospheric deposition, industrial activities, waste incineration and actual use. Even if the concentrations found are low, they can still represent a risk through ingestion, inhalation and dermal contact.

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