

POLYCHLORINATED BIPHENYLS AND POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS FROM DANUBE DELTA

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Abstract

Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), are highly hydrophobic and lipophilic. This makes them prone to accumulating in the environment and posing a risk to wildlife and human health. PCBs and PAHs can enter the environment through the dredging of waterways. This study aimed to determine the extent of PCB and PAH contamination in soil samples collected from the Danube Delta region. The samples were collected at different depths from six locations and the contaminants were extracted from soil with hexane/acetone and determined by gas and liquid chromatography. The results show the presence of the lower chlorinated biphenyls, PCB 28 and PCB 52, with concentrations which exceed in 16.6% of the samples even the intervention threshold of 0.01 mg/kg for PCB 52. Anthracene and phenanthrene were the 3-ring PAHs, contributing 58.3% of the total PAHs concentration.

Key words: soil, PCBs, PAHs, contamination.

INTRODUCTION

Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) exhibit properties that contribute to their persistence and bioaccumulation in the environment: high stability, low vapor pressure, and strong affinity for fats and oils (lipophilicity). This behaviour makes them potentially hazardous to human health (Edgar et al., 2003; Notarianni et al., 1998). For all these reasons the EU Regulation 2019/1021 stipulates the obligation to reduce and monitor the environmental emission in air, water and soil. PCBs have very high chemical stability, high electrical resistance, low volatility and resistance to degradation in the presence of high temperatures (Sandu et al., 2013). All these properties have led to numerous industrial applications. As a result, PCBs have been used as dielectric fluids in capacitors and transformers, as hydraulic fluids in mining equipment, as heat transfer fluids or for vacuum pumps ("closed" uses); they were also used in the production of plasticizers and additives, cement, lubricating and cutting oils, as well as printing inks ("open" or "dissipative" uses) (Niu et al., 2022). The main source of PCBs is industrial activity (Sandu & Virsta,

2015). However, dredging waterways also represents a significant source of these pollutants. Dredging generates substantial amounts of sediment and soil highly contaminated with PCBs. This contamination results from the historical discharge of large amounts of PCBs into aquatic environments and their tendency to be strongly absorbed by sediments and soil (Combi, 2016).

Characterized by their fused aromatic ring structures, polycyclic aromatic hydrocarbons (PAHs) encompass a vast array of compounds with varying levels of environmental persistence and toxicity. The arrangement of these rings, whether linear, angular, or clustered, influences their individual properties and behaviour in the environment.

These compounds are divided into low molecular weight (LMW-PAHs) with less than 4 aromatic rings in molecule and high molecular weight (HMW-PAHs) with more than 4 aromatic rings (Abdel-Shafy & Mansour, 2015).

PAHs originate from both natural and anthropogenic sources. Natural sources of PAHs include forest fires and volcanic eruptions. However, the primary source of PAHs is incomplete combustion from human activities. This includes industrial processes

such as waste incineration, metal production (iron, steel, aluminum), cement and asphalt manufacturing, and power generation. Other significant contributors include vehicle emissions (cars, trucks, diesel engines), coal gasification, and the production of coal-tar pitch, dyes, rubber tires, and pesticides (Abdel-Shafy & Mansour, 2015; Srogi, 2007). As observed by Ravindra et al. (2008), mobile emission sources, including aircraft, ships, trains, and off-road vehicles, have been identified as a significant contributor to PAH emissions.

In their 2014 study, Wenning and Martello observed a distinct gradient in PAH concentrations within aquatic environments, with the highest levels occurring in sediments, followed by biota, and the lowest levels in the water column.

MATERIALS AND METHODS

Twelve soil samples were collected on three depths from four profiles carried out in two drained and dammed agricultural sites situated in the Danube Delta, named Dunăvăț and Carasuhat. Dunăvăț area has 2538 ha, less than 40% of it have been used in agriculture since 1985. Carasuhat has 3380 ha of which 84.7% were used in agriculture. The extent of the agricultural area on this surface has been significantly diminished since 2008 because of the renaturation process. The soils are mainly Fluvisols (Gleyic-calcaric subtype), Gleysols (Calcaric Fluvic and Calcaric Fluvic Mollic Gleysols subtypes) and Histosols (Terric and Thionic subtypes) (Munteanu, 1996; Calciu et al., 2023). The soils classified after WRB (2014) were grouped according to the strength of the histic character (Mocanu et al., 2023). Soil samples were obtained from two profiles established in each location: P1 D and P2 D from Dunăvăț, P1C and P2C from Carasuhat (Figure 1). The coordinates of each location were recorded using a GPS device.

To gain a comprehensive understanding of the extent of PCB residue contamination in the selected study areas, a total of 14 soil samples were collected from the vicinity of the profiles at two different depths. PCBs and PAHs are analyzed from soil according to the standards set forth in the European Standards (EN

17322:2022 and EN 17503:2022, respectively). To extract these compounds from soil, a Soxhlet extractor and a mixture of hexane and acetone (in a 1:1 ratio) were employed.

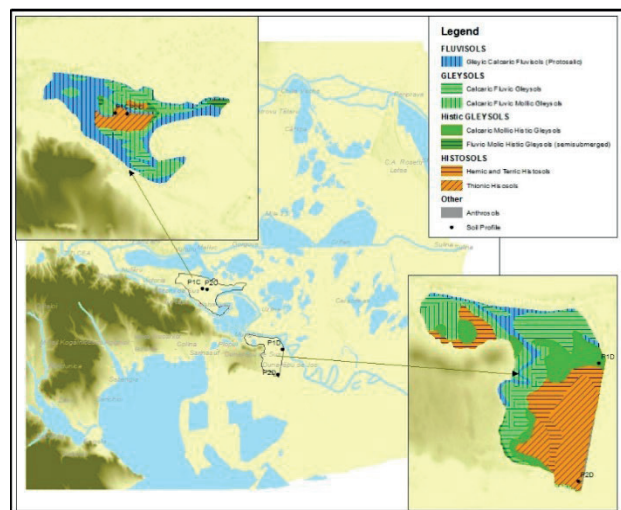


Figure 1. Map of the soil samples collected from Dunăvăț and Carasuhat profiles

The extract is washed with water for chromatography to remove acetone and it is passed through anhydrous sodium sulphate. If necessary to remove the sulphur, copper powder can be used.

The analysis focused on seven indicator polychlorinated biphenyls (PCBs), specifically PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, and PCB 180, as specified in Order 756/1997. These PCBs were measured using an Agilent gas chromatograph (GC), an instrument that separates chemical mixtures, equipped with an electron capture detector (ECD), which is highly sensitive to PCBs. The separation was conducted on a long and narrow capillary column (30 meters in length, 0.32 millimeters in diameter, and 0.25 millimeters in thickness), equipped with a nonpolar stationary phase (DB-5). This approach proved effective in differentiating and resolving the diverse isomeric structures of polychlorinated biphenyls. The determination of PAHs was performed on a Knauer ultrahigh pressure liquid chromatograph (UHPLC) with UV-VIS detection, at 254 nm.

In accordance with Order 756/1997, the following priority PAHs are to be quantified: anthracene, benzo(a)anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene, chrysene,

fluoranthene, indeno(1,2,3)pyrene, naphthalene, and phenanthrene, as well as pyrene. The pair consisting of benzo[ghi]perylene and indeno(1,2,3)pyrene cannot be determined with this type of detector. The separation of the other compounds was performed with a C18 column (2.1 mm x 100 mm x 1.8 μ m) operated at 40°C.

The mobile phase is composed of water and acetonitrile and the gradient of this mobile phase is presented in Table 1.

To minimize the contamination, all the glassware is rinsed with hexane, acetonitrile and acetone. To ensure the accuracy and reliability of the results, quality control and quality assurance procedures included duplicate samples, blank samples, and analysis of a certified reference material were used.

The limit of quantification for each PCB isomer is 1 μ g/kg and for PAHs ranged from 0.02 mg/kg to 0.05 mg/kg.

Table 1. Flow and gradient of the mobile phase

Time (minute)	Flow (ml/min)	Acetonitrile (%)	Water (%)
0	0.4	50	50
1.6	0.4	55	45
2.9	0.4	60	40
3.7	0.4	70	30
8.5	0.4	85	15
13	0.4	50	50

Physico-chemical parameters used for characterization of soil samples and the appropriate analytical methods are:

Soil reaction (pH) - potentiometric method, in water suspension, SR-7184-13;

Organic carbon (C, %) - wet oxidation, method Walkley-Black modified by Gogoășă, STAS 7184/21-82;

Mobile phosphorus (P_{AL} , mg/kg) - Egner-Riehm-Domingo method, STAS 7184/19-82;

Conductometric residue (EC, μ S/cm) - Aqueous extract and conductometric determination, STAS 7184/7-87;

Nitrate (N-NO₃, mg/kg) - potentiometric method, ICPA methodology;

Bulk density (g/cm³) - analyses on core sampler (cylinder method);

Particle size fraction (mm) - wet and dry sieving, sedimentation procedure, pipette sampling, followed by chemical treatment with

different dispersant agents (H₂O₂, HCl, Na₄P₂O₇·10H₂O) according to organic matter and carbonate content.

RESULTS AND DISCUSSIONS

PCBs content

The results for the total concentration of PCBs obtained from the four sampling locations (P1D, P2D, P1C, and P2C) in Dunăvăț and Carasuhat are shown in Table 2. The average total PCB concentration exceeds the established threshold of 0.01 mg/kg. Even the maximum value of the total concentration is ten times lower than the alert threshold (0.25 mg/kg).

Table 2. Median, minimum and maximum concentration for the sum of PCBs in Dunăvăț and Carasuhat soil profiles

	Σ 7PCBs (mg/kg)		
	Medium	Minim	Maxim
Dunăvăț	0.010	0.003	0.010
Carasuhat	0.011	0.004	0.025
Normal value	<0.01 mg/kg		
Alert threshold	0.25 mg/kg		
Intervention threshold	1 mg/kg		

Regarding the profile of the isomers, at the first depth (0-20 cm) the low chlorinated isomers have the largest contribution to the total concentration (Figure 2).

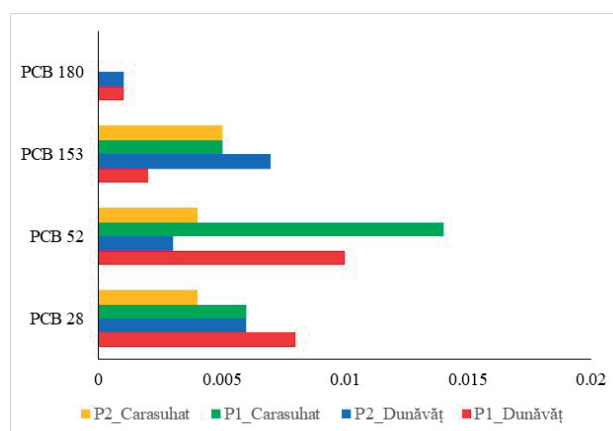


Figure 2. PCBs profiles in 0-20 cm soil samples collected from Dunăvăț and Carasuhat

Thus, PCB 52 isomer (tetrachlorobiphenyl) contaminates all the samples averaging 0.004 mg/kg. 25% of the analysed soil samples have concentrations between the upper limit of

the normal value (<0.0001 mg/kg) and alert threshold (0.002 mg/kg), 58.4% exceed the alert threshold and 16.6% exceed even the intervention threshold (0.01 mg/kg).

PCB 28 also contaminated all the samples with an average of 0.003 mg/kg. Analysis of the soil samples revealed that 25% had PCB concentrations falling between the upper limit of the normal range (<0.0001 mg/kg) and the alert threshold (0.002 mg/kg), while 75% exceeded the alert threshold.

Tetra- and pentachlorinated biphenyls (PCB 101 and PCB 118) were not highlighted in any of the samples analyzed.

Of the two hexachlorinated isomers (IUPAC numbers 138 and 153), only PCB 153 was detected. The average concentration of PCB 153 was 0.005 mg/kg, exceeding the upper limit of the normal value (<0.0004 mg/kg) but remaining below the alert threshold of 0.01 mg/kg. Heptachlorobiphenyl (PCB 180) was found in only 4 out of 12 soil samples, with concentrations approximately (0.001 mg/kg), which is well below the alert threshold. Similar results were observed in Yangtze River Delta where PCB 52 was identified as the most abundant congener in soil (Sun et al., 2016).

The observed PCB profile, with its high percentage of PCB 52, suggests potential contamination with Aroclor 1254, a PCB mixture historically used in paints and sealants (Cachada et al., 2009).

The peculiarity of this type of pollution comes from the fact that the Danube, which passes through 13 countries and 4 capitals, encounters many sources of pollution. Thus, it transports pollutants such as PCBs and PAHs that are strongly adsorbed by sediments and implicitly by soils from the delta.

While local sources likely contribute to PCB contamination, the long-range atmospheric transport and deposition of PCBs, particularly those with lower molecular weights, cannot be ruled out as a contributing factor (Meijer et al., 2003).

Regarding the variation of the PCB isomers on the soil profile an important decreased in the concentration is observed (Figures 3 and 4). Even if the profile of the isomers is the same, a 10-fold decrease can be observed between the soil samples collected from the first depth and those collected from the third depth.

The concentrations of PCB isomers in soil samples collected from areas situated near Dunăvăț and Carasuhat are presented in Table 3 and Table 4. It can be observed again the presence of low chlorinated PCB, especially PCB 28 (trichlorobiphenyl) and PCB 52 (tetrachlorobiphenyl). PCB 101 and PCB 118 (pentachlorobiphenyls) contaminate samples for Nufăru-Rusca and Matita Rusca with concentration which exceed the upper limit of the normal value (<0.0004 mg/kg) but they do not reach the alert threshold (0.01 mg/kg). PCB 138 and PCB 153 exhibited a similar pattern of exceedance. PCB 28 concentrations exceeded the alert threshold of 0.002 mg/kg in 75% of the soil samples, while PCB 52 exceeded this threshold in all analyzed samples.

The other isomers do not make an important contribution to the total concentration of PCBs. The concentration of penta-, hexa-, and heptachlorinated byphenyls is lower or slightly exceeds the upper threshold of normal values. So, the contamination with low chlorinated isomers of PCB in Dunăvăț and Carasuhat is not an accidental one.

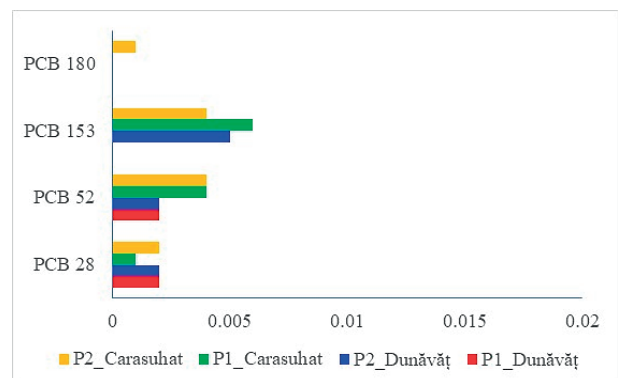


Figure 3. PCBs profiles 20-30 cm soil samples collected from Dunăvăț and Carasuhat

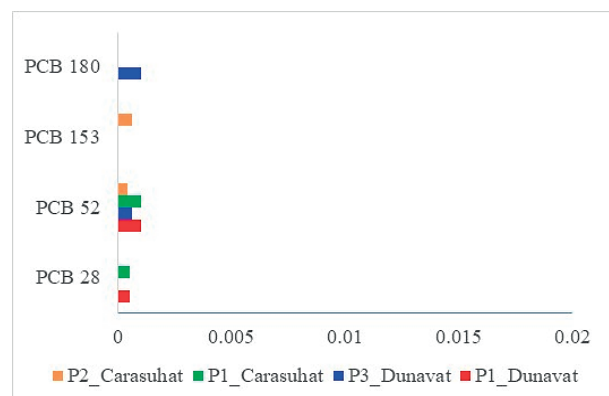


Figure 4. PCBs profiles in soil samples collected from 30-40 cm

Table 3. Concentration of PCBs in soil samples collected from Nufăru-Rusca, Candura and Matita Roșca

PCB isomers	Nufăru-Rusca		Candura		Matita Rosca	
	0-28 (cm)	28-38 (cm)	0-20 (cm)	20-42 (cm)	0-20 (cm)	20-40 (cm)
PCB 28	0.003	0.006	0.009	blq	0.003	0.005
PCB 52	0.011	0.009	0.015	0.008	0.015	0.013
PCB 101	blq*	0.001	blq	0.003	blq	blq
PCB 118	blq	0.001	blq	blq	0.001	blq
PCB 138	0.007	blq	blq	blq	blq	blq
PCB 153	0.007	0.005	blq	blq	blq	blq
PCB 180	blq	blq	blq	blq	blq	blq

Table 4. Concentration of PCBs in soil samples collected from, Dovnica, Carasuhat-Zaharcu and Caraorman

PCB isomers	Dovnica		Carasuhat-Zaharcu		Caraorman	
	0-28 (cm)	28-38 (cm)	0-20 (cm)	20-42 (cm)	0-20 (cm)	20-40 (cm)
PCB 28	0.001	0.003	0.006	blq	0.003	0.002
PCB 52	0.011	0.009	0.014	0.008	0.015	0.008
PCB 101	0.002	0.001	blq	blq	0.005	0.001
PCB 118	0.001	blq	0.001	blq	blq	blq
PCB 138	blq	blq	blq	0.001	0.007	0.007
PCB 153	blq	0.001	0.005	0.003	blq	0.002
PCB 180	blq	blq	blq	blq	blq	0.002

blq* - below limit of quatification (1µg/kg)

PAHs content

The average concentration of the total PAHs in Dunăvăt and Carasuhat soil profiles is 0.103 mg/kg, value that slightly exceeds the upper threshold of normal value (<0.1 mg/kg) according to Order 756/1997. The PAHs profile in soil depending on the number of aromatic rings is shown in Figure 5.

Three-ring PAHs (anthracene and phenanthrene) were the dominant components in the soil samples, contributing 58.3% of the total PAH concentration. This finding aligns with observations by Jia et al. (2021), who also reported a predominance of 3-ring PAHs in their study.

The 5-ring PAHs (benzo(b)fluoranthene and benzo (k)fluoranthene) contaminate only two samples collected from Dunăvăt (P1).

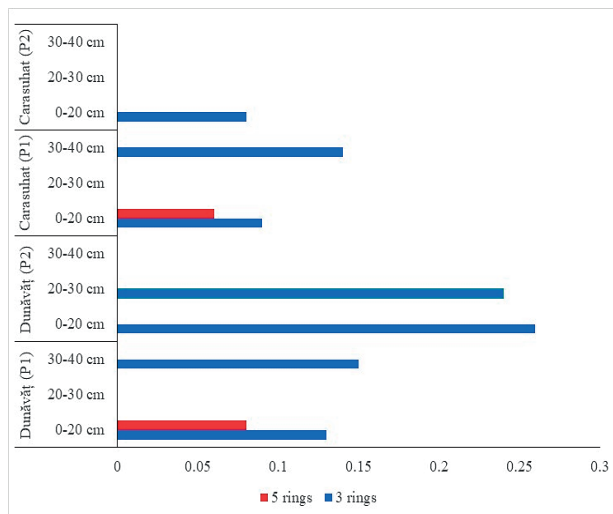


Figure 5. PAHs profile in soil samples collected from Dunăvăt and Carasuhat

Phenanthrene, a persistent and toxic polycyclic aromatic hydrocarbon (PAH), is widely distributed in both aquatic and terrestrial environments, where it poses significant risks to organisms (Al-Saad et al., 2019).

The dominance of low molecular weight PAHs (LMW-PAHs), indicated by a $\sum\text{LMW-PAHs}/\sum\text{HMW-PAHs}$ ratio greater than 1, suggests that petroleum combustion is a major contributor to PAH contamination in these soils (Al-Saad et al., 2019). Naval traffic and industrial emissions likely contribute to the PAH burden in the study area's soil.

The total concentration of PAHs in the top layer (0-20 cm) is higher in the 20 -30 cm layer in Dunăvăt (P2) and Carasuhat (P2) which leads us to think at atmospheric deposition. In Dunăvăt (P1), the higher PAH concentration at the 30-40 cm soil depth compared to the topsoil may be attributed to soil mixing processes.

To explain the behaviour of different PCB and PAH isomers, soil physical and chemical properties were examined.

Physical soil properties indicate high clay content (over 50%), but bulk density values characterize these soils as highly porous and non-compacted soils (Table 5).

As a result, this kind of soils are very permeable, allowing nutrients, pesticides and other pollutants to easily flow toward the ground water (Păltineanu et al., 2022). From this point of view these soils are under potentially severe risk (Mocanu et al., 2023).

Table 5. Physical properties of soil sample collected from Dunăvăț and Carasuhat

Identification		Bulk density (g/cm ³)	Particle size fraction (mm)			
Location	Depth (cm)		Coarse sand	Fine sand	Silt	Clay
			2.0-0.2	0.2-0.02	0.02	<0.002
P1_Dunăvăț	0-20	1.10	0.0	7.4	29.9	62.7
	20-30	1.15	0.0	10.3	27.4	62.3
	30-40	1.11	0.1	8.5	25.1	66.3
P2_Dunăvăț	0-20	0.63	0.8	0.4	31.8	67.0
	20-30	0.59	0.5	3.1	38.5	57.9
	30-40	0.27	0.9	20.9	23.7	54.5
P1_Carasuhat	0-20	0.80	1.1	10.0	24.4	64.5
	20-30	0.76	1.4	5.1	28.3	65.2
	30-40	1.11	0.1	14.2	35.8	49.9
P2_Carasuhat	0-20	0.44	3.0	6.7	33.2	57.1
	20-30	0.40	0.8	15.5	30.6	53.1
	30-40	0.34	0.1	2.4	35.7	61.8

Analysis of the collected soil samples revealed significant variability in chemical properties, as shown in Table 6. Soil pH values ranged from highly acidic (5.09) to moderately alkaline (8.03), with no significant correlation observed between pH and PCB concentrations. This finding is consistent with observations reported by Niu et al. (2022).

Table 6. Chemical properties of soil sample collected from Dunăvăț and Carasuhat

Identification	Depth (cm)	pH	C (%)	N-NO ₃ (mg/kg)	P _{AL} (mg/kg)	EC (μS/cm)
P1_Dunăvăț	0-20	8.03	3.57	9	47	278
	20-30	7.69	3.71	10	47	875
	30-40	7.54	4.63	45	38	2910
P2_Dunăvăț	0-20	5.09	15.4	67	29	4380
	20-30	4.94	21.7	152	29	3440
	30-40	5.62	28.0	274	14	4360
P1_Carasuhat	0-20	6.23	9.53	38	48	1607
	20-30	6.38	9.11	40	54	1810
	30-40	7.11	5.05	17	29	1204
P2_Carasuhat	0-20	6.42	13.5	24	229	2020
	20-30	6.64	11.8	23	163	1961
	30-40	6.95	12.6	17	67	656

Regarding the correlation between PAHs concentrations and pH, it can be observed that a higher level was obtained in P2 Dunăvăț, where pH is ranged between 4.94 and 5.62. Pawar in 2015 noticed that pH 7.5 is the most suitable value for the degradation of PAHs. Adsorption on the soils of phenanthrene at pH 5.0 was higher than in those at pH 6.2 and 7.5, which may be related to alteration of the hydrophobic

character of humic substances. The same phenomenon was observed by Ping and Luo in 2019.

Soil organic matter is considered an essential factor affecting the accumulation of PCBs and PAHs in soil. High organic matter content can strengthen the binding of PCBs and PAHs to soil particles and thus prolong their persistence. In many studies, the concentration of PCBs was found to be positively proportional to soil organic matter (Ren et al., 2019; Xu et al., 2019). There are also studies in which its concentration correlates with organic content but with an inverse trend (Di Guardo et al., 2020). The lack of correlation between soil organic carbon and PCB congeners suggests that factors beyond organic carbon content, such as the continuous deposition of contaminated sediments, may influence PCB distribution in the Danube Delta. In contrast, PAH concentrations appear to be strongly influenced by organic carbon content, with higher organic carbon levels associated with greater PAH accumulation. This observation is supported by similar findings reported by Du et al. (2022).

Another important parameter which influences the total concentration of PAHs is nitrate. Nitrate act as an electron acceptor and it plays a significant role in the oxidation of PAHs. A report stated that the metabolism of PAHs with three and four rings was significantly facilitated after nitrate addition (Yang et al., 2018). Another study showed that phenanthrene degradation decreased under nitrogen addition in phenanthrene-spiked soil (Johnson & Scow, 1999). In this study, nitrate was positively correlated with PAH concentrations, respectively with the phenanthrene concentration.

The PCBs isomer content in soil does not seem to be correlated with nitrate content.

The nutrients seem to be another important parameter which influence the PAHs content in soil. Thus, with the supplementing of nutrients the total PAHs concentration in the soils were reduced by 34% (Du et al., 2022). The higher content of phosphorus was reported in Carasuhat (P2) where the concentration of the PAH compounds was the lowest.

The electrical conductivity of the soil solution is a basic indicator reflecting the fertility characteristics of the soil. The US Department

of Agricultural's Salt Reform Laboratory proposed that soil with an EC higher than 4000 $\mu\text{S}/\text{cm}$ should be regarded as salinized soil, because excessive salt content affects soil respiration and crops (Yingbin et al., 2016).

In Dunăvăț and Carasuhat the electrical conductivity ranged between 278 $\mu\text{S}/\text{cm}$ and 4380 $\mu\text{S}/\text{cm}$. The highest value is P2 Dunăvăț where PAHs concentration is the biggest. Instead, PCBs concentration in P2 Dunăvăț is smaller than in Carasuhat, so it seems that PCBs content is negatively correlated with electrical conductivity. Same results were obtained by Niu et al. in 2022 which found that proportion of low chlorinated PCBs decreased with the increasing of soil conductivity.

CONCLUSIONS

The total PCB concentration in the soil samples from Dunăvăț and Carasuhat ranged from (0.012 to 0.018 mg/kg), slightly exceeding the normal threshold of 0.01 mg/kg but remaining well below the alert threshold of 0.25 mg/kg. Analysis of the PCB homologue profile revealed a predominance of low-chlorinated biphenyls, particularly PCB 52 (tetrachlorinated biphenyl) and PCB 28 (trichlorobiphenyl). This pattern of contamination, with a focus on PCB 28 and PCB 52, was consistent across all soil samples collected from areas near Dunăvăț and Carasuhat.

The average concentration of the total PAHs is 0.103 mg/kg, a value that slightly exceeds the upper threshold of normal value (<0.1 mg/kg).

The 3-ring PAHs (anthracene and phenanthrene) were dominant contributing 58.3% of the total PAHs concentration.

The contamination source with PCBs could be associated with Aroclor 1254 which has a high percentage of PCB 52 and was used especially in paints and sealants.

$\sum\text{LMW-PAHs}/\sum\text{HMW-PAHs}$ is greater than 1, so there the major source of PAHs contamination in Dunăvăț and Carasuhat might be combustion processes.

Correlation between soil organic content and PCB congeners was not evident, instead PAHs content was positively correlated with organic carbon content, electrical conductivity and

nitrate and negatively correlated with phosphorus content.

Pollution with PCBs and PAHs comes from the fact that the Danube encounters many sources of pollution. Thus, it transports pollutants such as PCBs and PAHs that are strongly adsorbed by sediments and implicitly by soils from the delta.

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