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BEHAVIOUR OF POLYCHLORINATED BIPHENYLS CONTAMINATING SOIL NEAR ZADAR

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This study analysed PCB-contaminated natural soil excavated from an area adjacent to an electrical transformer station in Zadar, Croatia. For one year, PCB concentrations were measured in the soil and leachate water under natural climatic conditions. After 12 months, a negligible quantity of Aroclor 1248 (0.024 % in average) and a total of seven key PCB congeners (IUPAC No: PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153, and PCB-180) were leached through the soils into water collected under lysimeters (0.032 % in average). Although the amounts of leached PCBs were relatively small, their range $2 \mu\text{g L}^{-1}$ to $15 \mu\text{g L}^{-1}$ substantially exceeds the maximal allowed concentration of total PCBs in fishponds which is 1 ng L^{-1} .

Soil samples were taken on two occasions from three depths from each lysimeter. The distribution of total PCBs as Aroclor 1248 equivalents and seven individual PCB congeners was determined within soil layers before and after planting seeds. In all soil plots the content of total seven PCBs and some individual PCB congeners in the surface soil layers significantly decreased. The total content of the seven PCB congeners in the surface soil layer of all soil plots decreased between 19.0 % (soil plot 2) and 47.6 % (soil plot 1) and in the middle soil layer between 8.1 % (soil plot 4) and 37.4 % (soil plot 1). PCB-28 and PCB-52 showed the highest percent of removal in all soil plots after 12 months of the experiment. The most important mechanism of removal of "lighter" congeners may be evaporation from the soil surface. Generally, our results showed that the PCBs accumulated in the deepest level of the soil, probably due to vertical transport and decreased evaporation. Some of the PCB content was lost to their degradation in the rhizosphere of the plants growing on the analysed soil plots.

KEY WORDS: *Aroclor 1248, ETS Zadar, leachate water, lysimeters, PCB congeners*

In 1991, a capacitor of an electrical transformer station (ETS; I/O: 110/35 kV) was damaged during military aggression on Zadar, Croatia, which led to a spill of oil containing polychlorinated biphenyls (PCBs). The analysis of samples collected around the ETS showed substantial levels of PCBs, which raised concern about the risk of contamination of underground waters of this limestone area (1-4). A number of studies have been carried out to see the efficiency of phytoremediation as a form of bioremediation, for it is known that plants in symbiosis with the micro flora of the rhizosphere can degrade xenobiotics in soil (5,6). Plants are known

to degrade, accumulate, adsorb and evaporate a variety of contaminants (7-10). In terrains exposed to precipitation, contaminants are transported deeper into the soil, eventually reaching water. The aim of this study was to determine the extent of this transport around the ETS Zadar over a year and under natural climatic conditions.

MATERIALS AND METHODS

Soil sampling and PCB extraction

The study included samples contaminated naturally by PCBs. Soil was sampled from around the concrete

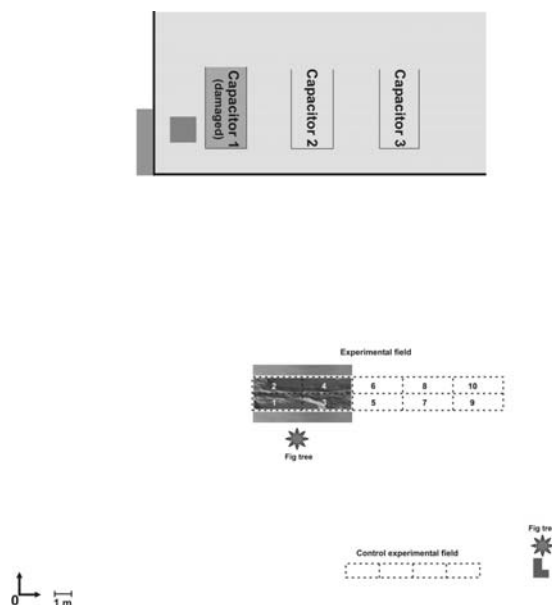


Figure 1 Position of the experimental field in relation to the damaged electrical transformer station in Zadar

foundation of the damaged ETS capacitor. Samples were cleared of rocks and plants and homogenised in a concrete mixer for about three hours. The homogenised samples were then distributed in ten wooden, bottomless boxes placed near the ETS to make soil plots (11). This study included the first four soil plots (Figure 1).

Each plot had three lysimeters, each for one layer of PCB-contaminated soil (Figure 2). At the beginning of the experiment, soil samples were taken from three layers, one for each lysimeter: the surface layer (0 cm

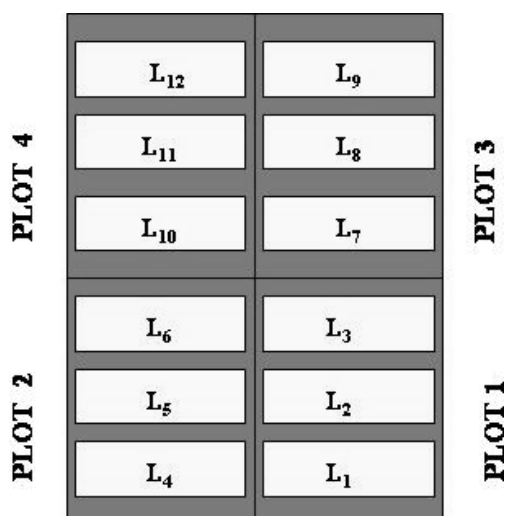


Figure 2 Distribution of lysimeters in the experimental plot

to 5 cm), middle layer (5 cm to 10 cm), and the deep layer (10 cm to 15 cm) to determine the distribution of PCB mass fractions before planting seeds. One year later, when the plants grew, we repeated the sampling. However, as the soil had settled, each layer now shrunk for 1 cm. Additionally, we took soil samples from around plant roots (rhizosphere).

Lysimeters

The lysimeters (70 cm x 70 cm x 20 cm) were made of stainless steel and placed in the soil plots at an angle to allow water to collect in bottles. Each lysimeter ended with a screen and a 10 cm extension connecting it to a 10 L collection bottle. To exclude the effects of sunlight, the collection bottles were kept in wooden containers dug in at the depth of 70 cm from the surface (Figure 3). At the beginning of the experiment, every collection bottle was added a mixture of *n*-hexane and methanol (3:1, respectively) and 1 L of tap water. Every lysimeter was filled with a 5 cm layer of gravel (to improve the passage of water) and topped with a 15 cm layer of homogenised contaminated soil.

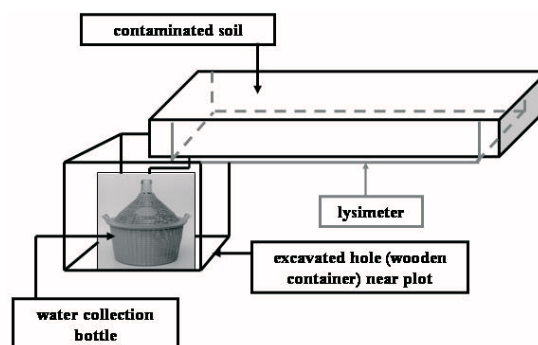


Figure 3 The position of a lysimeter in relation to a collection bottle

Seeds were planted in September 2004. The first soil plot was planted with alfalfa (*Medicago sativa* L.), the second with a mix of commercial grass adapted for the dry Mediterranean climate (the Adriatic mix), and the third with thale cress, that is, *Arabidopsis thaliana* (L.) Heynh. The fourth plot with its native flora served as control.

PCB analysis in soil samples and leachate water

Soil samples were dried at room temperature and passed through a 2 mm sieve. PCBs were extracted from each sample three times with *n*-hexane/acetone solvent mixture (1:1) using an automated extraction system (ASE 200 Extractor; Dionex, USA) at 373 K

and pressure of 14 MPa. Extraction was repeated with the extracts and n-hexane fractions were purified further (12).

Leachate water was collected after precipitations. Due to substantial particle content, it was filtered using a filter paper (Filtrak; 21 N) before analysis. We used n-hexane/acetone solvent mixture (1:1) for solid phase extraction from the filter paper in an ultrasonic bath (2x30 min). Before extraction, NaCl was added to the filtrate, which was then saturated with HCl (36 %) to obtain pH=2. PCBs were duplicate extracted in separation funnels with 100 mL n-hexane.

The analytical method used to purify the obtained extracts included filtration through a Na₂SO₄ column (anhydrous Na₂SO₄) and purification through an Al₂O₃ column. Eluates were analysed using an Agilent Technologies 6890N network GC system gas chromatograph equipped with a ⁶³Ni electron capture detector and a 30 m x 320 μm HP-5 hires glass column (5 % phenylmethylsiloxane) and 0.25 μm film thickness. The carrier gas was nitrogen. The experimental conditions of the instrument were: injector temperature 523 K, detector 623 K, temperature programme of the column oven 333 K to 503 K. The software used was ChemStations Rev. A.08.03 [847] for the GC Agilent 6890 series of gas chromatographs. Detailed descriptions of these methods can be found elsewhere (13-15).

PCB stability testing in leachate water over a month

PCB stability in leachate water was tested in order to determine the quantity of PCBs (Aroclor 1248 equivalents) that remained in glass bottles after one month, under natural, field conditions.

Each test was done in triplicate. Glass funnels were filled with a layer of gravel and a layer of uncontaminated soil from the surrounding area, and placed over glass bottles to repeat the field conditions with lysimeters as closely as possible. Five litres of tap water was passed through the funnels and the glass bottles added 5 μg of Aroclor 1248 in n-hexane/methanol (3:1) solution. The bottles with the Aroclor 1248 and funnels were then placed in wooden containers and left for a month.

RESULTS AND DISCUSSION

A layer of soil (0 cm to 20 cm) was sampled from the location of the ETS Zadar for mechanical and

chemical analysis. The soil texture is classified as clay loam (Table 1). Judging by the pH in 1 mol L⁻¹ KCl, the reaction was alkaline and the soil was humus-rich. Correlating to the humus content, the total nitrogen was high, and so were the physiologically active phosphorus and sodium (Table 2).

Table 1 Mechanical profile of the soil adjacent to the damaged electrical transformer station in Zadar

Soil particles diameter / mm	<0.002	0.002 to 0.02	0.02 to 0.05	0.05 to 0.2	0.2 to 2.0
Soil particles / %	37.0	16.6	20.9	13.3	10.4

Table 2 Chemical profile of the soil adjacent to the damaged electrical transformer station in Zadar

pH		Humus / %	Total N / %	mg kg ⁻¹	
H ₂ O	1 mol L ⁻¹ KCl			P ₂ O ₅	K ₂ O
7.7	7.3	4.5	0.23	438	389

PCB stability in leachate water was tested under natural climatic conditions over one month of the winter and the summer. Figure 4 shows the means of the remaining PCB content in all bottles, expressed as Aroclor 1248 equivalents and as the sum of seven key PCB congeners: PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 i PCB-180 after staying in bottle for one month of the summer and of the winter. The figure clearly shows that PCB loss was greater in the summer month than in the winter month.

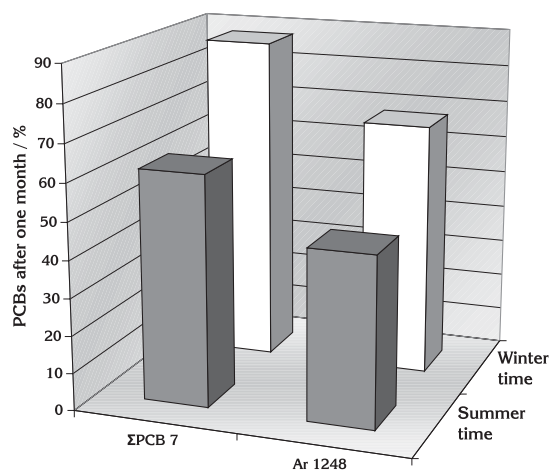


Figure 4 The remaining PCB content expressed as Aroclor 1248 equivalent and total seven PCB content after one month in the summer and winter

Figure 5 shows the total concentration of the seven key PCBs in leachate water of each soil plot after two

raining periods of different intensity. Water collected in the first raining period includes three days (17-20 October 2004), and as many as 25 days of the second period (27 January – 21 February 2005). Raining intensity is shown to greatly influence the leaching intensity and the level of PCB in leachate water.

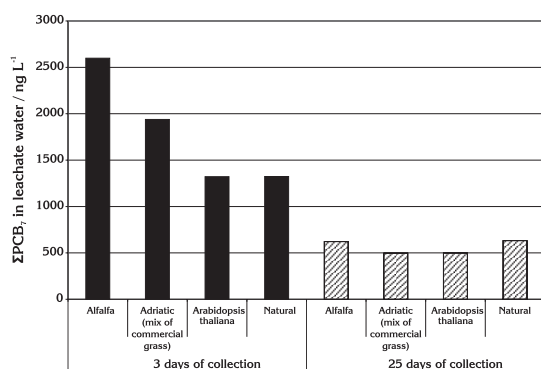


Figure 5 Total seven PCB concentrations in leachate water per soil plot over two raining periods of different intensity

Figure 6 shows total PCB concentrations in leachate water expressed as Aroclor 1248 equivalents. It covers two irrigation periods during drought and seven raining periods (before and after planting seeds, respectively). The first irrigation was performed in one soil plot, and the PCB concentration in the leachate water is expressed as the arithmetic mean of concentrations measured in three lysimeters. The second irrigation included two soil plots, and the PCB concentration is expressed as the arithmetic mean of PCBs measured in the leachate waters of six lysimeters. PCB concentrations for each raining period are the arithmetic means and standard deviations of PCB concentrations measured in leachate waters of 12 lysimeters. The analysis of leachate water after the first irrigation with tap water (in July 2004) showed

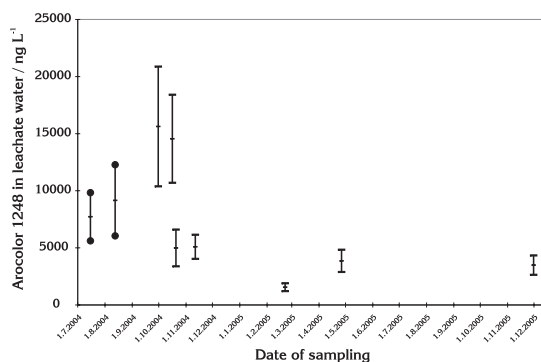


Figure 6 Aroclor 1248 concentration in leachate water after irrigation (●-●) and raining period (|-|)

7726 ng L⁻¹ of total PCBs expressed as Aroclor 1248, whereas the concentration after the second irrigation (in August 2004) was 9164 ng L⁻¹.

Total PCB concentration in leachate water after the first raining period (13-30 September 2004) was (15632±5245) ng L⁻¹ and after the second raining period (30 September – 16 October 2004) (14556±3857) ng L⁻¹. In these periods PCBs were unevenly distributed between leachate waters collected in different lysimeters, which is accounted for by still unsettled soil in the early phase of the experiment (16-18). The concentrations of total PCB in leachate water collected after this initial stage was rather even, save for the February 2005 measurement, that showed somewhat lower values [(1555±345) ng L⁻¹]. Figure 7 shows the total concentrations of seven PCBs in leachate water. The sequence of Aroclor 1248 concentration measured in the same samples corresponds to the concentration sequence of the total seven PCBs after the raining periods, but is reverse with respect to PCB finding after irrigation. The total concentration of seven PCBs in leachate water after the first irrigation was (2640±611) ng L⁻¹ and after the second irrigation it dropped a little to (1786±335) ng L⁻¹.

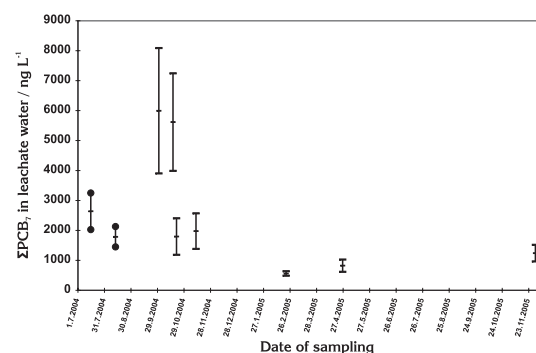


Figure 7 Total seven PCB concentrations in leachate water after irrigation (●-●) and raining periods (|-|)

Figure 8 shows the total content of leached PCBs by individual soil plot over 12 raining periods (13 September 2004 - 26 April 2005), expressed as Aroclor 1248 equivalents. For the irrigation water and six raining periods (13-30 September 2004, 1–16 October 2004, 17-20 October 2004, 21 October-11 November, 27 January-21 February 2005, 8-26 April 2005) the PCB content was measured in laboratory, and for the remaining six raining periods it was assessed from meteorological data on precipitation volume and the most recent PCB measurement in leachate water relative to the raining period. Over

nearly a year a relatively small amount of Aroclor 1248 (about 0.24 ‰) and total seven PCBs (about 0.32 ‰) was leached with rain from the thin layer of contaminated soil. The amount of leached PCB-28 was 0.34 ‰, of PCB-52 0.28 ‰, and of PCB-101, PCB 138 and PCB-180 about 0.23 ‰ (19).

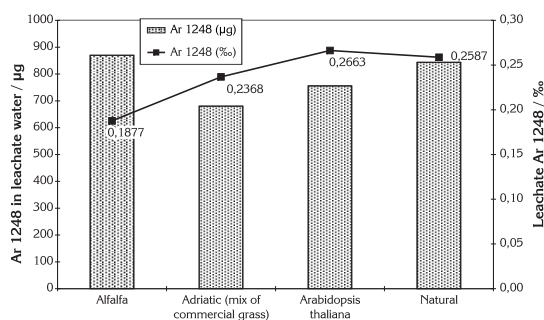


Figure 8 Total amount of Aroclor 1248 in leachate water after 12 raining periods (13 Sep. 2004 – 26 Apr. 2005)

In the first year of the experiment soil was sampled on two occasions, first in June 2004 (before planting seeds) and then in June 2005 (after the plants had grown). Table 3 shows PCB loss from separate layers of all soil plots over a year. The loss is calculated as the difference between the means measured in the first and second sampling. The PCB level expressed here is the arithmetic mean of PCB measurements in soil samples taken from three lysimeters. After 12 months, we observed a significant decrease of PCB content in the soil of plot 1. In the surface layer, total Aroclor 1248 dropped by 23.3 % and in the rhizosphere by 27.9 %. The drop was also significant for total seven PCBs for all layers in all soil plots (ranging from 2.5% to 47.6%).

Table 3 PCB loss (%) from the soil over one experimental year

Soil layer	Loss of ΣPCB_7 / %			
	Soil plot 1 Alfalfa	Soil plot 2 Adriatic mixture	Soil plot 3 Arabidopsis thaliana	Soil plot 4 Native flora
Surface	47.6	19.0	24.6	31.7
Middle	37.4	18.7	15.6	8.1
Deep	32.3	22.3	3.6	14.5
Rhizosphere	41.5	29.4	2.5	19.6

Figure 9 compares the mass fractions of the total seven PCBs by soil layer and plot between the two samplings. Mass fractions are expressed as the means of measurements taken from three lysimeters per plot.

The initial levels of the total seven PCBs in plot 1 were significantly higher than in other plots. The level of total seven PCBs in the surface layer was $(15.7 \pm 0.3) \times 10^6$, in the middle layer $(14.9 \pm 1.1) \times 10^6$, and in the deep layer $(13.5 \pm 0.3) \times 10^6$. The findings for the remaining three plots were comparable (about 11.3×10^6).

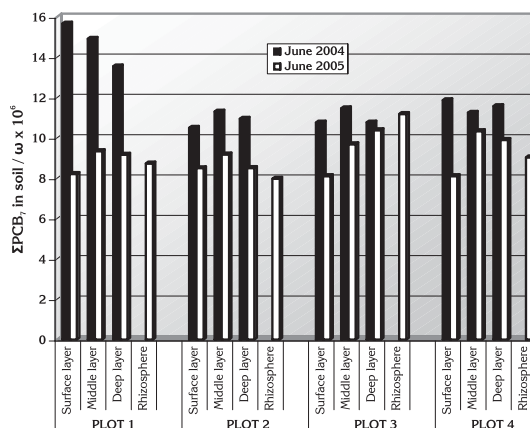


Figure 9 Total seven PCB mass fractions per soil layer after in two samplings

All plots showed a significant decrease in total seven PCBs in the second sampling, especially plot 1. However, the loss of total seven PCBs was smaller in the deeper layers of soil; in fact, this is where they concentrated due to vertical transport (Figure 10).

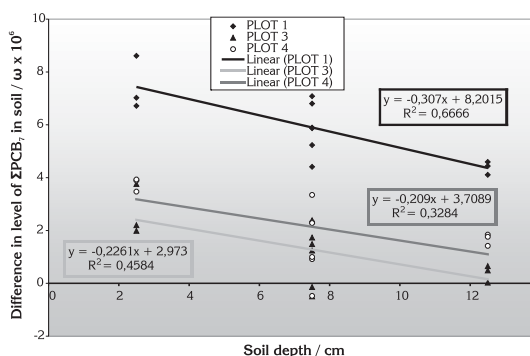


Figure 10 The relation between total seven PCB loss and soil depth

Looking at the loss of PCB-28 in the first year of experiment with respect to depth of soil layers, we observed that it was greater in layers closer to the surface than in the deeper layers (with the exception of samples taken from plot 2) (Figure 11). This is probably due to the volatility of PCB-28 that is, some of it evaporated into the atmosphere.

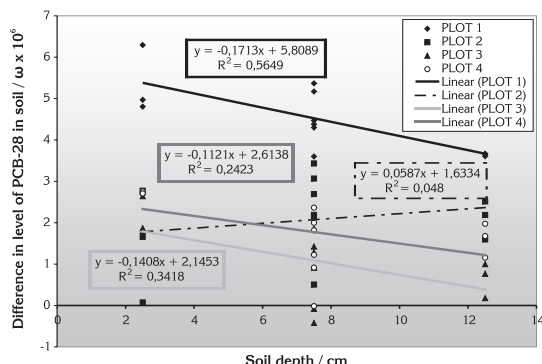


Figure 11 The relation between PCB-28 loss and soil depth

CONCLUSION

The test of PCB stability in leachate water has shown that a greater amount of PCB congeners (especially more volatile ones) is lost in the summer than in the winter. These losses however do not affect an objective insight into the rate of PCB leaching with water. As the leachate water was collected over periods much shorter than a month, our findings of the PCB leaching rate are pretty realistic. PCB levels measured in the initial collection periods (September 2004) were unevenly distributed between the soil plots, most likely because the soil had not settled by that time. In addition, PCB levels in leachate water largely depend on precipitation intensity.

After 12 months we observed that only small amounts of Aroclor 1248 (0.24 % in average) and total seven PCBs (0.32 % in average) were leached through a relatively thin layer of soil. An average of 0.34 % of PCB-28 and 0.28 % of PCB-52 passed through the soil. Even though the quantities are relatively small, in view of the maximal allowed concentration of total PCBs in fishpond water of 1 ng L⁻¹ PCB concentrations in leachate waters, ranging from 2 μg L⁻¹ to 15 μg L⁻¹, are more than substantial.

Our results show that the level of total seven PCBs decreased in the surface layer of all soil plots (ranging from 19.0 % to 47.6 %). In the middle layer this drop ranged between 8,1 % and 37.4 %, and in the deep layer between 3.6 % and 32.3 %. This in general points to an accumulation of PCBs in the deepest soil layer, which is probably the result of vertical transport of contaminants from the upper layers of soil and diminished evaporation in the deeper layers.

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Sažetak**PONAŠANJE POLIKLORIRANIH BIFENILA (PCB) U ZAGAĐENOM TLU NA PODRUČJU ZADRA**

U ovom radu korišteno je prirodno tlo zagađeno s PCB-ima. Tlo je iskopano oko uništenog kondenzatora trafostanice Zadar (ETS 110/35 kV). Eksperiment je proveden pod prirodnim klimatskim uvjetima tijekom jedne godine, kako bi se mjerila razina PCB-a u tlu i procjednim vodama. Pokusna površina sastoji se od 4 gredice. Na svakoj gredici postavljena su tri lizimetra. Nakon 12 mjeseci (12 perioda u sakupljanju procjednih voda) relativno male količine Aroclora 1248 (prosječno 0,024 %) i sume 7 ključnih kongenera PCB-a (IUPAC No: PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 i PCB-180) nađene su u procjednoj vodi (prosječno 0,032 %). Međutim, ukoliko se uzme u obzir da su maksimalno dopuštene razine PCB-a u ribogojilištima 1 ng L^{-1} , razine izmjerene u procjednim vodama u rasponu od $2 \mu\text{g L}^{-1}$ do $15 \mu\text{g L}^{-1}$ su više nego značajne.

Tijekom dva uzorkovanja analizirano je tlo sa svakog lizimetra na tri dubine. Prije i poslije sijanja biljaka istraživana je raspodjela ukupnih PCB-a tj. sadržaj Aroclora 1248 i pojedinačnih sedam ključnih PCB-a unutar analiziranih slojeva. U površinskom sloju tla svih gredica uočeno je značajno smanjenje sume sedam ključnih PCB-a i pojedinih kongenera PCB-a. Nakon 12 mjeseci, najveći postotak smanjenja zagađivala određen je u tlu gredice br. 1. Rezultati ukazuju da se sadržaj sume sedam ključnih PCB-a u površinskom sloju tla svih gredica smanjio i taj gubitak je u rasponu od 19,0 % (gredica br.2) do 47,6 % (gredica br.1). U srednjem sloju tla gubitak sume sedam ključnih PCB-a je u rasponu od 8,1 % (gredica br.4) do 37,4 % (gredica br.1). Tijekom pokusa u tlu svih gredica uočen je najveći gubitak PCB-28 i PCB-52. Jedan od glavnih mehanizama odgovornih za gubitak niže kloriranih kongenera PCB-a iz površinskog sloja tla je hlapljenje. Općenito, rezultati ukazuju na povišene razine PCB-a u dubljim slojevima tla u odnosu na površinski sloj, vjerojatno zbog vertikalnog transporta PCB-a i manjeg hlapljenja. Osim toga, određeni gubitak PCB-a sigurno je i posljedica njihove razgradnje u rizosferi nađenog biljnog pokrova istraživane zemljišne pokusne površine.

KLJUČNE RIJEČI: Aroclor 1248, ETS Zadar, lizimetri, kongeneri PCB-a, procjedne vode

REQUESTS FOR REPRINTS:

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